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THE CAPTURE OF ELECTRONS BY ALPHA-PARTICLES

By Arthur H. Barnes
Physics Laboratories, Columbia University

(Received December 24, 1929)

Abstract

A stream of electrons is superposed upon a beam of alpha-particles. The alpha-particles are then deflected by a magnetic field and counted by the scintillation method. Alpha-particles which have captured electrons will not be deflected to the point where observation is made, and consequently, the decrease in scintillations will indicate the number of captures which occur.

Probability of capture as function of relative velocity.—It is found that electrons are captured when their velocity equals that of the alpha-particle, and also, at a series of discrete velocities both greater and less than that of the alpha-particle. Counting scintillations due to singly charged particles showed that at certain of these discrete velocities one electron is captured. At the other velocities two electrons are captured. This was determined by counting scintillations due to neutral particles which had passed undeflected through the magnetic field. Both single and double capture occur at zero relative velocity, the latter predominating as the electron density is increased.

Calculation of the kinetic energy of the electron with respect to the alpha-particle corresponding to each of the velocities at which single capture occurs, gives a series of energy values which can be associated with the energy levels in the ionized helium atom. Similarily, for the case of double capture, the sum of the kinetic energies due to each of the two electrons, corresponds to the energy of the quantum states of both the parhelium and orthohelium types of atom. There is indication that the hitherto unobserved ground state of orthohelium is being formed. The conclusion is reached that in order for capture to occur, it is necessary that the electron, due to some external field, possess a kinetic energy, which, with respect to the nucleus, is either zero, or equal to the energy of one of the quantum states of the atom. In the latter case double the normal energy must be radiated, and the question arises as to whether it is radiated as two quanta of normal frequency, or as one quantum of twice that frequency.

There is evidence that the *penetrating power* of the singly charged and neutral particles is less than that of the nucleus alone.

Time required for capture of electron by alpha-particle.—The construction of one of the tubes used permitted the time during which the alpha-particle was in the electron stream to be made less than 3×10^{-10} sec without appreciably decreasing the percent of capture. The electron density under these conditions was of the order of 10^7 electrons per cc.

IN A previous report[1] an experiment was described which showed that an electron is captured by an alpha-particle only at definite relative velocities.

[1] Bergen Davis and A. H. Barnes, Phys. Rev. **34**, 152 (July 1, 1929).

The series of energy values associated with these velocities was shown to correspond to the energy levels in the ionized helium atom.

The present paper gives the details of the experiment (which were omitted in the preliminary announcement) and presents additional information obtained with a new experimental arrangement.

First Experimental Tube

Two experimental tubes were constructed. The first tube is shown diagrammatically in Figure 1. The alpha-particle source is polonium deposited upon a pointed copper rod placed at *S*. A thin glass window *W*, 0.0005 cm thick, allows the alpha-particles to enter the tube. By thus placing the radioactive source outside the tube, contamination difficulties were entirely avoided.

After passing through the tube, the alpha-particles leave it by means of another window placed at *Y*, or if a sufficient magnetic field be applied at *M*, they will be deflected and pass out through a window at *Z*. The latter windows are each 0.001 cm thick. Zinc sulphide screens are placed outside the windows. Aluminum foil 0.0004 cm thick was placed before each screen to shield it from the light of the filament. The air is exhausted from the spaces between screen and window and also from the space between source and window.

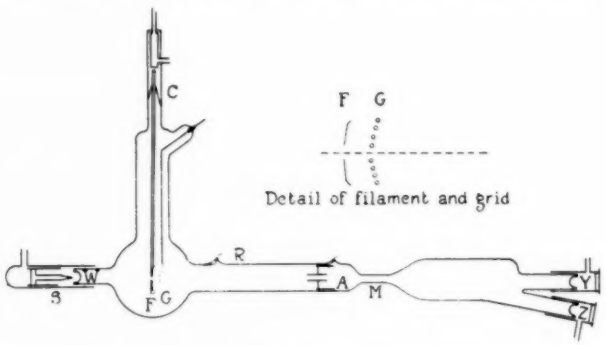

Fig. 1. Diagram of first experimental tube. *S*, radioactive source; *W*, thin glass window; *F*, filament; *G*, grid; *R*, lead to silvered surface; *A*, second anode; *M*, magnetic field; *C*, copper seals; *Y*, and *Z*, zinc sulphide screens.

The source of the electrons is a large oxide-coated filament *F*, 2.5 cm square and made slightly concave. A hole 0.5 cm in diameter allows the alpha-particles to pass through. The current necessary to heat the filament was about 150 amperes and entered the tube through water-cooled copper seals at *C*.

The first anode *G*, is placed one cm from the filament and takes the form of a conical spiral of 60 mil tungsten wire. The diameter of the inner and outer turn is 0.4 cm and 2.5 cm respectively. The spacing between turns is 0.4 cm. The second anode *A*, is a nickle cylinder 0.5 cm in diameter and 3 cm long. It is placed 18 cm behind the grid *G*.

The inside of the glass vessel is silvered and the conducting layer grounded to prevent accumulation of charge on the walls. All metal parts were outgassed in a vacuum furnace before being placed in the tube. The tube was evacuated, baked, and sealed off.

Electrons leaving the filament are accelerated to any desired velocity by the potential impressed upon the grid G. Due to the shape of the grid and filament, those electrons which pass through the grid will converge and proceed along the axis of the tube towards the anode A. The alpha-particle does not enter into a region of relatively great electron density until it reaches the point of convergence of the electron stream. If an electron is captured at this point, the alpha-particle will arrive at the magnetic field with a decreased charge, and consequently will not be deflected to the lower screen at Z. The decrease in scintillations observed at Z will therefore determine the number of captures which occur.

Procedure and Results

The procedure followed with this tube was to vary the magnetic field until the alpha-particles were deflected to the lower screen Z. The potential applied to the grid G, and cylinder C, was then varied in small steps and the corresponding change in the number of alpha-particles arriving at Z was determined. During most of the runs the current to G was 60 milliamperes and to A, 0.08 milliamperes.

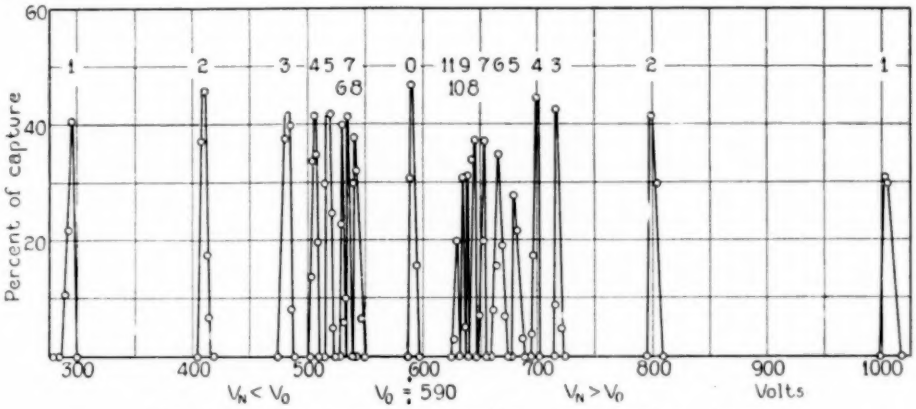

Fig. 2. Electron capture as a function of accelerating voltage.

It was found that capture takes place when the velocity of the electron is equal to that of the alpha-particle also at a series of definite electron velocities both greater and less than that of the alpha-particle. A curve showing the relation between capture and applied voltage as obtained with this tube is given in Figure 2. It consists of a double series of sharp maxima grouped on each side of a central peak. The velocity of the electrons corresponding to the voltage at which the central peak occurs is 1.44×10^9 cm/sec. This agrees closely with the calculated velocity of the alpha-particle after passing through the window of the tube.

If v is the velocity of an electron and u the velocity of an alpha-particle, then the kinetic energy of the electron with respect to the alpha-particle will be,

$$W = (\tfrac{1}{2})m(v-u)^2$$

where m is the mass of the electron.

Let V_n and V_0 be the potential differences through which electrons must fall to acquire the velocities v, and u, respectively, then,

$$eV_n = mv^2/2$$

and,

$$v = (2eV_n/m)^{1/2}$$

similarly,

$$u = (2eV_0/m)^{1/2}$$

substituting,

$$W = \left(\frac{1}{2}\right)m\left(\frac{2e}{m}V_n - \frac{4e}{m}V_n^{1/2}V_0^{1/2} + \frac{2e}{m}V_0\right)$$

$$= e(V_n^{1/2} - V_0^{1/2})^2$$

or,

$$\frac{W}{e} = (V_n^{1/2} - V_0^{1/2})^2 = E_n$$

where E_n is the energy expressed in volts when V_n and V_0 are in volts.

If in this equation we substitute for V_0 the voltage which will accelerate an electron to a velocity equal to that of the alpha-particle, and for V_n successively the voltages at which the observed peaks occur, then we arrive at a series of energy values which correspond to the energy levels in the ionized helium atom.

Table I gives the voltages of the observed peaks and the corresponding values of E_n. The last column gives the values of E_n as calculated from Bohr theory. There are of course two sets of observed values for E_n corresponding to the two cases in which $V_n > V_0$ and $V_n < V_0$.

TABLE I. *Values of E_n for which capture takes place.*

n	$V_n < V_0$	E_n	$V_n > V_0$	E_n	Mean of E_n	$E_n = 54.16/n^2$
1	295	50.6	1005	54.9	52.0	54.16
2	410	16.7	800	15.6	16.2	13.54
3	483	5.33	720	6.45	5.67	6.01
4	505	3.29	700	4.71	4.00	3.38
5	519	2.28	681	3.27	2.77	2.16
6	531	1.56	667	2.41	1.98	1.50
7	535	1.34	653	1.59	1.46	1.10
8	538	1.19	645	1.23	1.21	.84
9			638	.96		.67
10			635	.88		.54

It thus appears that the probability that an alpha-particle will capture an electron is great only when the kinetic energy of the electron with respect to the alpha-particle is either zero, or equal to the energy of one of the quantum states of the ionized helium atom. It is to be noted that the kinetic energy here referred to is that due to the applied field only.

The effect of varying the potential of the second anode A, with respect to the first G, was investigated. It was found that if the potential of A was made greater or less than that of G, then to maintain the condition for capture, it was also necessary to change the potential of G. Thus if the potential of A is decreased, then to maintain capture, it is necessary to increase the

potential of G. Another result of making the potential of A different from that of G is a considerable broadening of the peaks, especially when A is at a higher potential than G. These effects indicate that capture is taking place at some point between the first and second anodes, and that the velocity of the electrons is the governing factor.

It will be noticed that the peaks do not continue to the central peak as they might be expected to do, but stop abruptly at about the tenth energy level. It was thought that this might be due to re-ionization caused by collisions with the molecules of residual gas in the tube. This effect was investigated with the second tube and will be discussed later.

An alpha-particle which has picked up one electron will be deflected to the lower screen Z, when the magnetic field is doubled. If it has picked up two electrons it will pass through the magnetic field without deflection and arrive at the upper screen Y. It should therefore be possible to observe an increase in scintillations corresponding to every decrease.

When this procedure was tried no increase could be detected. It was further found that with the magnetic field entirely removed, a decrease in scintillations on the upper screen occurred at the same voltages at which decreases had formerly occurred on the lower screen. This effect indicated that the penetrating power of a singly charged or neutral particle was less than that of the nucleus alone.

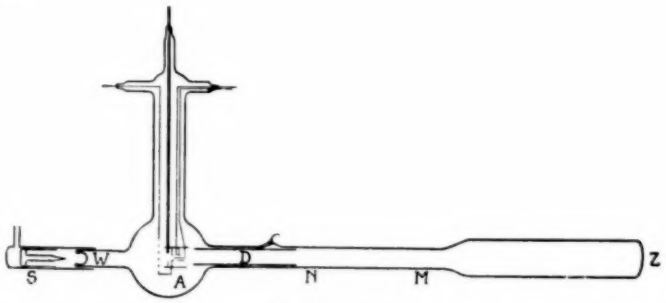

Fig. 3. Diagram of second experimental tube. S, radioactive source; W, thin glass window; A, filament-anode system; M, magnetic field; Z, zinc sulphide screen.

Second Experimental Tube

The second tube was constructed with four objects in view.

1. The reduction of the time of passage of an alpha-particle through the electron stream to a known small value.
2. The detection of scintillations due a singly charged and neutral particles.
3. The investigation of the effect of varying the velocity of the alpha-particle.
4. The investigation of the captureless intervals located on each side of the central peak.

The construction of the second tube is shown diagramatically in Figure 3 and Figure 4. The electron source is an oxide-coated filament F, in the form of a flat disk with a 0.4 cm diameter hole at its center to allow the passage of the alpha-particles. Two mm in front of the filament is placed a plate P, with

0.5 cm diameter hole exactly opposite the hole in the filament. A 60 mil tungsten wire T, extends for one cm along the axis of the tube to a point within one mm of the plate P. Surrounding the wire is a cylinder C, 0.5 cm in diameter and 0.5 cm long. A second cylinder D, 2 cm in diameter and 10 cm long is placed 1 cm behind the first cylinder and on the same axis. The whole assembly is held rigidly in place and mutually insulated. Separate leads are brought out from each of the elements.

Zinc sulphide is placed on the inside of the flattened end of the tube at Z. The window used to admit the alpha-particles was of very nearly the same thickness (0.0005 cm) as that used on the first tube, so that the velocity of the alpha-particles in each tube was very nearly the same. The tube was evacuated and sealed off.

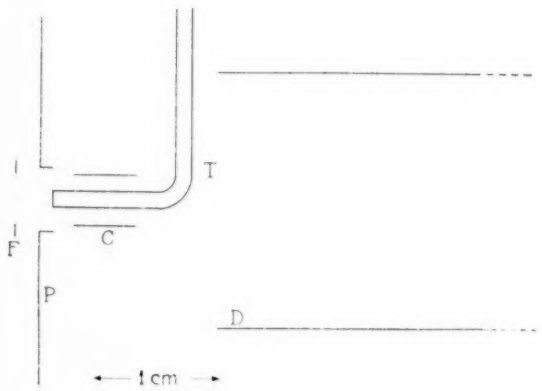

Fig. 4. Detail of filament-anode system in second tube. F, filament; P, plate; T, wire; C, cylinder; D, cylinder.

If the anode assembly (P, C, D, and T) is all put at the same potential the electrons leaving the filament will be accelerated by the field between the filament and the plate P, and wire T. Some will pass between this wire and the cylinder C, and so on to the larger cylinder at D. If however, the cylinder C, is put at filament potential, the field existing between C and T will be sufficient to deflect all the electrons which pass P, to the wire T near its end. The length of path which the electrons can possibly travel is thus limited. Furthermore every electron which reaches the wire T, must cross the paths of the alpha-particles.

Procedure and Results with Second Tube

The effect on capture of various arrangements of the anode system was tried. The plate P, wire T, and cylinders C, and D, were put at the same potential and the percent of capture determined. The cylinders C and D, were then put at filament potential and it was found that the percent of capture remained practically unchanged.

Under the latter conditions the greatest length of path possible for the electrons was approximately 5 mm, and since the velocity of the alpha-particle as it passes through this region is 1.45×10^{9} cm/sec it follows that the process of capture must take place in less than 3×10^{-10} sec.

In the second tube the scintillations due to both singly charged and neutral particles could be detected. It was possible to count the increase in scintillations due to alpha-particles which had captured one electron and therefore struck the screen at a point midway between the center and the edge. It was also discovered that at certain voltages neutral particles were produced. They, of course, were not deflected by the magnetic field and struck the center of the screen.

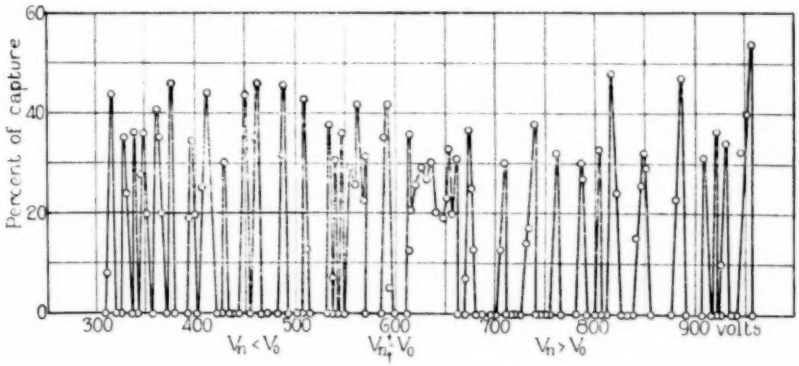

Fig. 5. Double electron capture as a function of accelerating voltage.

It was found by observing at the center of the screen that there exists a whole series of voltages at which double capture occurs. A curve showing the relation between this type of capture and the applied voltage is given in Figure 5. There exists also an independent series of values at which single capture occurs, (Figure 6.). With the first tube it was not possible to separate

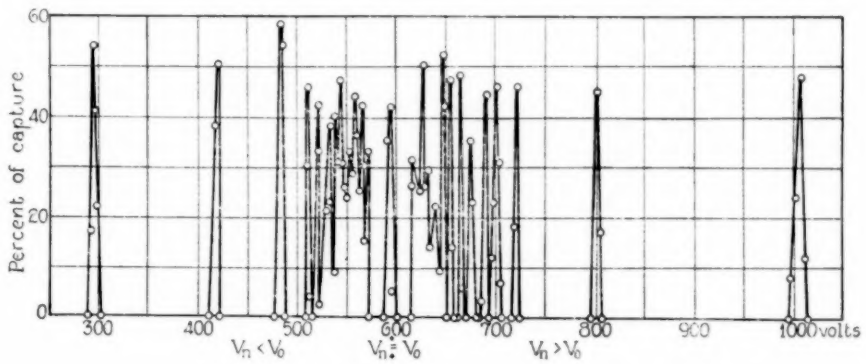

Fig. 6. Single electron capture as a function of accelerating voltage.

these two types of capture, (since only a decrease in scintillations could be observed) and consequently some of the peaks which were thought due to single electron capture were in reality due to double capture. The peak found at 410 volts for example was at first attributed to single capture. The second tube showed however, that this was a voltage at which double capture occured, and that the single capture peak was at 418 volts.

The most striking feature of the curves is the narrowness of the peaks. This indicates that capture takes place at a point where the electrons are moving with a very uniform speed and direction. The electron velocity at this point will in general be somewhat less than that corresponding to anode potential. The observed voltage across the tube will therefore not indicate the true velocity at the point of capture. This condition introduces an error in the determination of the location of the peaks and consequently also in the calculated energy values. It should be possible to design an arrangement in which the electron velocity at the point of capture was very exactly known and so obtain correct values for the energy levels.

The whole range of voltage was investigated and the single capture peaks separated from those due to double capture. A revised table showing single capture voltages and the corresponding energy values is given in Table II.

TABLE II. *Values of E_n for single capture.*

n	$V_n<V_0$	E_n	$V_n>V_0$	E_n	Mean of E_n	$E_n=54.16/n^2$
1	293	51.8	1005	54.9	53.3	54.16
2	418	14.8	800	15.6	15.2	13.54
3	481	5.53	719	6.45	5.99	6.01
4	508	3.16	700	4.71	3.93	3.38
5	519	2.31	689	3.72	3.01	2.16
6	531	1.56	673	2.69	2.12	1.50
7	535	1.39	662	2.02	1.70	1.10
8	540	1.12	652	1.51	1.31	.84
9	—	—	645	1.21	—	.67
10	—	—	637	.53	—	.54

Applying the energy relation given above to the case of the double capture peaks it is possible to calculate the kinetic energy of each electron with respect to the alpha-particle. If double capture takes place under conditions similar to that for single-capture, then the sum of the kinetic energies of each of the two electrons, (as acquired from the applied field, but with respect to the alpha-particle) should correspond to the energy of one of the quantum states of the helium atom.

Table III shows the voltages at which double capture occurs and the corresponding relative kinetic energy of one and of two electrons.

TABLE III. *Values of E_n for double capture.*

$V_n<V_0$	E_n	$2E_n$	$V_n>V_0$	E_n	$2E_n$	Mean of $2E_n$
315	43.0	86.0	955	43.5	87.0	86.5
327	38.6	77.2	930	38.4	76.8	77.0
338	35.4	70.8	921	36.0	72.0	71.4
347	32.1	64.2	907	33.6	67.2	65.7
360	28.4	56.8	885	29.7	59.4	58.1
375	25.0	50.0	848	24.1	48.2	49.1
395	19.5	39.0	815	18.0	36.0	37.5
410	16.4	32.8	803	16.4	32.8	32.8
428	13.0	26.0	783	13.5	27.0	26.5
448	10.5	21.0	760	10.8	21.6	21.3
460	8.25	16.5	738	8.2	16.4	16.5
486	4.60	9.20	708	5.3	10.6	9.90
507	3.24	6.48	672	2.60	5.20	5.84
533	1.49	2.98	661	1.96	3.96	3.47
537	1.25	2.50	652	1.51	3.02	2.76

The second value (77 volts) given in the last column of the table agrees with the observed total energy of the parhelium type of atom (54.2+24.5 volts). It is suggested that the first value, 86.5 volts, may correspond to the ground state of orthohelium, a configuration hitherto unobserved, but which might be formed under the special transition conditions peculiar to this experiment.

It is also probable that the remaining values constitute a double series, consisting of the energy levels of both the parhelium and orthohelium types.

No significance is to be attached to the fact that the peaks in Figures 2, 5, and 6, do not rise much above 50 percent. It was discovered after these curves had been taken that by a suitable adjustment of the position of the radioactive source it was possible to increase capture to over 90 percent.

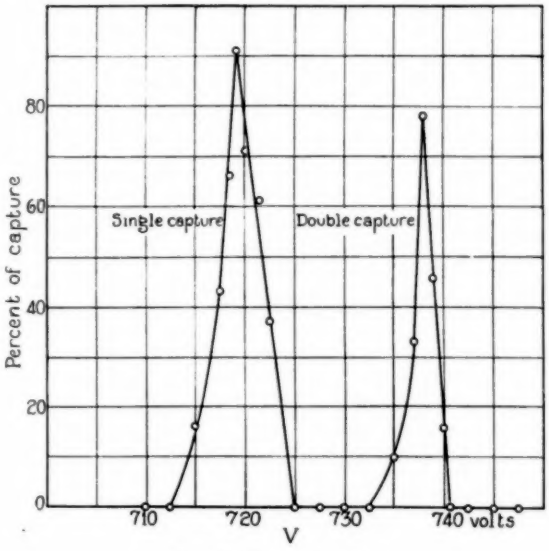

Fig. 7. Typical peaks.

Two typical peaks taken under these conditions are shown in Figure 7. The peak at 719 volts is one due to single capture. The 738 volt peak is due to double capture.

The explanation of this dependence of capture on the position of the source is that the electron stream is not uniformly distributed over the area through which the alpha-particles are passing. Thus, if there is always a portion of the observed alpha-particles which pass through a region where the electron density is always too low for capture to occur, it will be impossible by merely increasing the current to the anode to make the percent of capture rise above a certain value. If however, the position of the source is so adjusted that all the alpha-particles which fall within the field of view of the microscope, (2.4 mm in diameter) must pass through the region of maximum electron density, then by increasing the current to the anode it is possible to make capture approach 100 percent.

The effect of gradually increasing the current to the anode T, when the voltage is held at one of the peak values is illustrated in Figure 8 and Figure

9. The curve in Figure 8 is taken at the single capture peak at 719 volts. Figure 9 is the curve obtained at the double capture peak occurring at 738 volts.

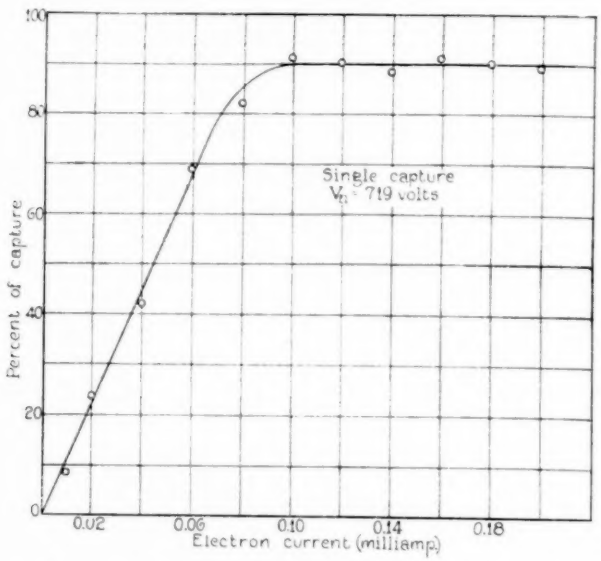

Fig. 8. Capture as a function of electron current. A curve taken at the 719 volt single capture peak.

Since these voltages are relatively close together, the electron density for a given anode current is probably not very different in each case, and there-

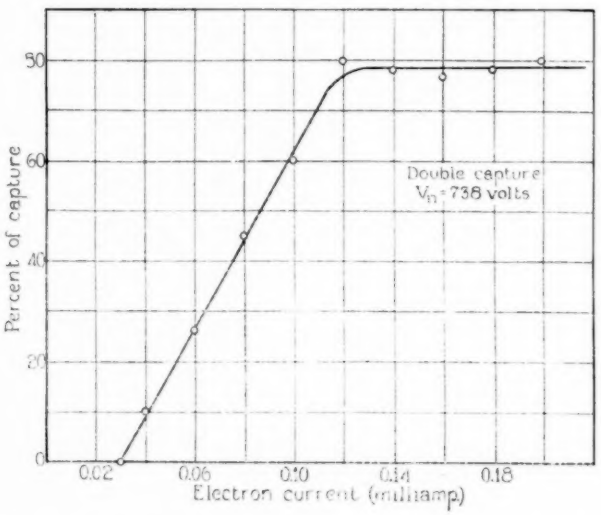

Fig. 9. Capture as a function of electron current. A curve taken at the 738 volt double capture peak.

fore the percentage of capture should be a rough indication of the relative probabilities of single and double capture.

Further information on this question is given in Figure 10 which shows a series of three curves taken at the 590 volt peak which corresponds to zero relative velocity of electron and alpha-particle. Curve (1) shows the manner in which the number of single captures varies with the current going to the anode T. It was obtained by counting increases in scintillations due to singly charged particles striking the screen at the midway point. Curve (2) shows the variation with current of the number of neutral particles which strike the screen at its center. Curve (3) shows the total decrease in scintillations as observed at the lower edge of the screen. The ordinates in this case are not given in percent but in the observed variation in scintillations per minute.

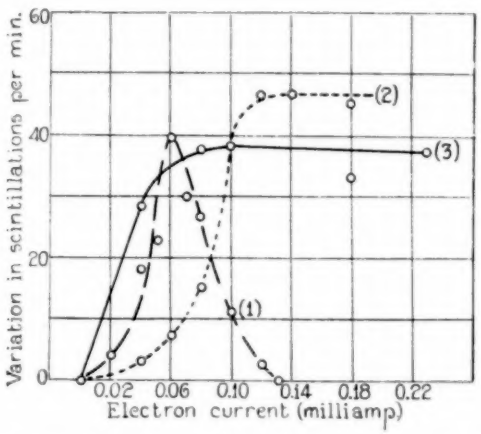

Fig. 10. Capture at zero relative velocity as a function of electron current. (1), single electron capture; (2), double electron capture; (3), total decrease of doubly charged alpha-particles.

For single capture, (Figure 8) saturation is reached when only 0.1 milliampere of current flows to the anode T. The order of magnitude of the electron density under these conditions is about 10^7 electrons per cc, which corresponds to an average distance between electrons of 4.6×10^{-3} cm. The process of capture must therefore involve some mechanism, which, when the energy condition is satisfied is effective over a relatively large region of space.

With the second tube it was possible to investigate the effect of reducing the velocity of the alpha-particles. Two different velocities were tried by interposing aluminum foil between the radioactive source and the window. The resultant velocities of the alpha-particles were 1.35×10^9 cm/sec and 1.21×10^9 cm/sec. The whole series of peaks was found to shift in each case. Several of the peaks were located in their new position and the corresponding energy levels calculated by means of the energy relation already given. A comparison of these values with the values found at the higher alpha-particle velocity showed very good agreement.

The intervals on each side of the central peak where no capture occurs were found to be much narrower with the second tube than with the first. Whereas with the first tube they were 40 volts wide, with the second they

were only about 22 volts wide. In other words capture terminated at the tenth energy level in the first tube and at about the fifteenth energy level in the second. If these captureless intervals were due to re-ionization by collision with the residual molecules of gas in the tube, then the width of the intervals should be dependent on the length of path between the point of capture in the electron stream and the magnetic field. To test this the magnet was placed in two positions along the tube at M, and at N, (Figure 3) such that the distance $(A-M)$ was double the distance $(A-N)$. It was impossible to detect any change in the width of the interval under these two conditions. These captureless intervals must therefore be due to some cause other than collisions of this kind.

Conclusion

In the type of recombination taking place in this experiment the electron does not fall from rest into a given energy level (except in the special case when the velocities of electron and alpha-particle are equal). It has an initial kinetic energy, due to the applied field, equal to that of the energy level at which it is captured. Twice the normal energy must therefore be radiated, and the question arises as to whether it is radiated as two quanta of normal frequency, or as one quantum of double that frequency.

The striking result of this experiment is the discovery that electron capture is governed by a definite energy condition. In order for capture to occur, it is necessary that the electron, due to some external field, possess a kinetic energy, which, with respect to the nucleus, is either zero, or equal to the energy of one of the quantum states of the atom.

It has been shown that electron capture takes place in less than 3×10^{-10} sec in a region where the electron density is probably not greater than 10^{7} electrons per cc. Probably the time involved is actually much less than this. The process of capture must therefore involve some mechanism whose action is extremely rapid, and when the energy condition is satisfied, effective over a relatively great region of space. When the energy condition is not satisfied the capture mechanism either does not function at all, or operates in such a manner that the probability of capture is relatively very small. The inference to be drawn is that under certain energy conditions, the mutually effective radius of action of the electron and the nucleus may be relatively very great, while under other energy conditions it is very small.

The results of this experiment are based upon the counting of over 700,000 alpha-particle scintillations.

In conclusion, the writer wishes to express his appreciation and gratitude to Professor Bergen Davis for suggesting this research, and for his continued interest and encouragement throughout the course of the experiment. Many thanks are also due to the other members of the department of Physics.

THE RELATIVE INTENSITIES OF SUPER-MULTIPLET LINES

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Abstract

A simple method is described by which one may construct wave functions for the case of (*jj*) coupling. The wave functions for $(2p)^2$, so determined, agree with those given in a previous paper, when one sets the electrostatic interaction equal to zero. It is shown how the ordinary multiplet intensity formulae may be modified to give the relative intensities in a super-multiplet for (*jj*) coupling. The modified formulae, applied to the transition $(2p)^2 \rightarrow 2p3s$, give relative intensities in agreement with those found in the above paper, for this limiting case. The sum-rules hold quite generally for non-equivalent electrons, and it is shown to what degree they hold for a transition such as $(2p)^2 \rightarrow 2p3s$.

ON THE basis of the Darwin-Pauli theory of the spinning electron it has been found possible[1,2] to calculate the relative intensities of super-multiplet lines for certain transitions, such as $(ds \rightarrow fs)$ and $(2p\ 2p \rightarrow 2p\ 3s)$. The intensities so found are dependent upon the strength of the electrostatic interaction between the electrons, as compared with that of the magnetic interactions between spin and orbital angular momenta. In the limiting case of strong electrostatic interaction, or $(1s)$ coupling, these intensities agree with those calculated from the formulae for relative intensities within an ordinary multiplet. In the other limiting case, that of (*jj*) coupling, where the spin-orbit interaction is predominant, analogous formulae can be set up and the intensities so obtained would agree with those found from more general formulae when the electrostatic interaction is set equal to zero. The difficulties involved in obtaining these general formulae for any degree of coupling have already been mentioned in a previous paper.[2] Accordingly, it seems expedient to calculate the theoretical intensities for the two limiting cases and to use some suitable method of interpolation when comparing with experiment.

1. The Wave Functions and Energy Value for (*jj*) Coupling

For simplicity, we shall at first deal with only two electrons. For (*jj*) coupling, we are to consider as a perturbation the magnetic interaction between each electron and its own orbit. Each electron can be considered

[1] W. V. Houston, Phys. Rev. **33**, 297 (1929).

[2] J. H. Bartlett Jr., Phys. Rev. **34**, 1247 (1929). A sign error in the matrix components of the intercombination lines should be corrected. Both c_1 and c_6 should have the opposite sign. None of the conclusions of the paper are invalidated, to our degree of approximation. Furthermore, in the roots ϵ_3 and ϵ_4, one should substitute $+8$ for -8.

separately during this perturbation calculation and then the product functions, or a linear combination thereof, will represent the total system. As usual, we group those functions together which have a common $m=\sum m_l+m_s$, where m_l and m_s refer to the projections of l and s, the azimuthal and spin quantum numbers, on a preferred axis. For an externally undisturbed system, terms with different m's cannot combine, since m represents a constant of the motion. The wave functions are written

$$\psi_\alpha{}^m = R_{ln}(r) P_l{}^{m-1/2} S_\alpha \; ; \quad \psi_\beta{}^m = R_{ln}(r) P_l{}^{m+1/2} S_\beta .$$

The two possible values of the spin variable are S_α and S_β respectively, and

$$P_l{}^{m_l} = (l-m_l)! \sin{}^{m_l}\theta \left(\frac{d}{d\cos\theta}\right)^{l+m_l} \frac{(-\sin^2\theta)^l}{2^l l!} e^{im_l\phi}.$$

Let

$$\gamma_{ln} = \frac{h^2}{16\pi^2}\frac{Ze^2}{m_0{}^2c^2}\int R_{ln}{}^2 \frac{1}{r^3} d\tau \quad \text{and} \quad \epsilon = \frac{\Delta E}{\gamma_{ln}} .$$

For the perturbation arising from the interaction between spin and orbit, the secular equation is:

$$\begin{vmatrix} m-\frac{1}{2}-\epsilon & (l-m+\frac{1}{2})^{1/2}(l+m+\frac{1}{2})^{1/2} \\ (l-m+\frac{1}{2})^{1/2}(l+m+\frac{1}{2})^{1/2} & -m-\frac{1}{2}-\epsilon \end{vmatrix} = 0.$$

The roots are $\epsilon_1 = l$ and $\epsilon_2 = -l-1$, and the corresponding wave functions are:

$$\psi_1{}^m = (1/2l+1)^{1/2}\left[(l+m+\tfrac{1}{2})^{1/2}\psi_\alpha{}^m + (l-m+\tfrac{1}{2})^{1/2}\psi_\beta{}^m\right]$$
$$\psi_2{}^m = (1/2l+1)^{1/2}\left[-(l-m+\tfrac{1}{2})^{1/2}\psi_\alpha{}^m + (l+m+\tfrac{1}{2})^{1/2}\psi_\beta{}^m\right].$$

One sees that, for the state l, $j = m_{\max} = l+\frac{1}{2}$ and for the state 2, $j = m_{\max} = l-\frac{1}{2}$.

The calculation thus far deals with coupling of the type $(s_1 l_1) = j_1$. In order to treat coupling of the type $(j_1 j_2) = j$ one must construct antisymmetric wave functions from products of functions such as $\psi_1{}^m$ and $\psi_2{}^m$. For instance, set[3]

$$\psi_{j_1 j_2}{}^m = (\tfrac{1}{2})^{1/2} \begin{vmatrix} \psi_{j_1}{}^{m_1}(1) \; ; \; \psi_{j_1}{}^{m_1}(2) \\ \psi_{j_2}{}^{m_2}(1) \; ; \; \psi_{j_2}{}^{m_2}(2) \end{vmatrix} .$$

If now, for a given m, the vectors j_1 and j_2 combine to give only one j, then the state is not degenerate for (jj) coupling and will be represented, except perhaps for a sign factor, by a function of the above type. Just as frequently, however, one finds a degeneracy and the correct wave functions for a given value of j are found by taking linear combinations, the coefficients being

[3] In the more general case of more than two electrons, the antisymmetric functions will have the determinant form. See J. C. Slater, Phys. Rev. (being published). The notation used above is similar to that of the paper to which reference is here made.

determined from a perturbation calculation, the electrostatic interaction between the electrons being the perturbation. This degeneracy is for a given set $(j_1 j_2)$ combining to give different j's. If one should take the wave functions for the same j, as determined by this process, but for different sets $(j_1 j_2)$, and repeated the process, this would give the correct wave functions for (ls) coupling. This is to be expected, since it should make no difference in which order the various perturbations are applied. In the previous paper,[2] the reverse order was employed, and the results agree, both for energy values and for wave functions.

The total energy of the two-electron system for (jj) coupling is given by

$$E = E(n_1 l_1) + \gamma_{l_1 n_1} \epsilon(j_1) + E(n_2 l_2) + \gamma_{l_2 n_2} \epsilon(j_2).$$

This agrees with the work of Goudsmit[4] if we make $\gamma = a/2$.

2. Selection Rules

Let us denote the set of quantum numbers $(nljm)$ by p. Then the matrix element for a transition involving two electrons will be a linear combination, in the zeroth approximation, of matrix elements of the type

$$z(p_1 p_2 ; p_3 p_4) \sim \delta(p_2 p_4) z(p_1 p_3) + \delta(p_1 p_3) z(p_2 p_4) - \delta(p_2 p_3) z(p_1 p_4) - \delta(p_1 p_4) z(p_2 p_3). \quad (1)$$

Thus, whether the coupling be of the (ls) (jj) type, as long as the wave functions are formed by the linear combinations of functions of the unperturbed system, then two-electron jumps are not permitted. This is true for any number of electrons, but only as a first approximation. According to Pauli's exclusion principle, no two electrons can have the same p and so, for any transition, we have only one term on the right-hand side of equation (1). Let this term be the first, i.e. $p_2 = p_4$. That is, for one of the two electrons, all four quantum numbers remain the same, and for the other, the ordinary selection rules hold. In the (jj) coupling case, therefore, j_1 can change by $0, \pm 1$ and j_2 does not change. If $p_1 = p_3$ instead, then $\Delta j_1 = 0$ and $\Delta j_2 = 0, \pm 1$.

3. Intensities

Consider the transition $(n_1' l_1' j_1' m_1' ; n_2 l_2 j_2 m_2) \rightarrow (n_1'' l_1'' j_1'' m_1'' ; n_2 l_2 j_2 m_2)$. The z-matrix will be a linear combination of a number of "unperturbed" z-matrices, which have the form $\int [R_{l_2 n_2}(2)]^2 r_2^2 dr_2 \int R_{l_1' n_1'}(1) R_{l_1'' n_1''}(1) r_1^2 dr_1 \int P_{l_1'}^*(1) z_1 P_{l_1''}(1) d\omega_1$ corresponding to the term $z(p_1 p_3)$ in Eq. (1). Thus, the radial integration gives a common factor and, since this is the only way in which the principal quantum numbers can enter, they have no influence on the relative intensities in a super-multiplet. It makes, therefore, no difference in the relative intensities as to whether the electrons are or are not equivalent. The equivalence is manifested, however, in the disappearance of certain states with the result that certain intensity sums are not proportional to statistical weights of the corresponding states.

[4] S. Goudsmit, Phys. Rev. **31**, 946 (1928).

For (jj) coupling, j_2 plays the same role as s, and j_1 the same role as l, respectively, in (ls) coupling. We can introduce a notation analogous to the Russell-Saunders notation, namely, ${}^r(j_1)_j$, where $r=2j_2+1$. The j_1 labels the valence electron, and r is the multiplicity. Even when the two electrons are equivalent, there is no ambiguity as to which is the valence electron, unless $j_1=j_2$. In this case one must double the intensity as calculated from the formulae to be given, to allow for the two possibilities.

The ordinary multiplet formulae can now be rewritten in terms of j_1 and j_2 instead of l and s. In the ordinary multiplet theory the statistical weight of an ${}^r(l)$ state is $r(ll+1)$, e.g. a ${}^3D$ state has a degeneracy of fifteen. For (jj) coupling, the statistical weight of an ${}^r(j_1)$ state is $r(2j_1+1)$, except for equivalent electrons with $j_1=j_2$, where it becomes $2rj_1$. The degeneracy of a ps ${}^4(1/2)$ state is eight, that for a $(2p)^2$ ${}^4(3/2)$ state is twelve, and that for a $(2p)^2$ ${}^4(1/2)$ the same as for $(2p)^2$ ${}^2(3/2)$, namely eight.

The formulae in terms of j_1 and j_2 follow:

$$\Delta_{j_1}=\pm 1 \qquad J_{-1}=G_jA^{\,j\ ,j_1}_{j-1,j_1-1}=\frac{c}{4jj_1}P(j,j_1)P(j-1,j_1)$$

$$J_0=G_jA^{\,j,j_1}_{j,j_1-1}=\frac{c}{4jj_1}\,\frac{2j+1}{j+1}P(jj_1)Q(jj_1)$$

$$J_{+1}=G_{j-1}A^{\,j-1,j_1}_{j\ ,j_1-1}=\frac{c}{4jj_1}Q(jj_1)Q(j-1,j_1)$$

$$\Delta j_1=0 \qquad J_0=G_jA^{\,j,j_1}_{j,j_1}=\frac{c}{4jj_1}\,\frac{2j+1}{j+1}\,\frac{2j_1+1}{j_1+1}R^2(j)$$

$$J\pm 1=G_jA^{\,j\ ,j_1}_{j-1,j_1}=G_{j-1}A^{\,j-1,j_1}_{j\ ,j_1}=\frac{c}{4jj_1}\,\frac{2j_1+1}{j_1+1}P(j,j_1)Q(j-1,j_1)$$

where

$$P(j)=(j+j_1)(j+j_1+1)-j_2(j_2+1)$$
$$-Q(j)=(j-j_1)(j-j_1+1)-j_2(j_2+1)$$
$$R(j)=j(j+1)+j_1(j_1+1)-j_2(j_2+1).$$

The A's are the squares of matrix elements. For any super-multiplet, or group of lines belonging to a transition such as $sp\rightarrow pp$, the value of C is the same for all lines. The sum of intensities form any state with equivalent electrons over all the states (with non-equivalent electrons) to which transitions can be made is, for a given super-multiplet, proportional to the statistical weight of the initial state. If these sums be taken horizontally, then in general the vertical sums will not be proportional to the corresponding statistical weights due to the exclusion of certain states which would be possible if the electrons were not equivalent.

As examples of applications of the formulae we give below the results (1) for a case with two non-equivalent electrons, and (2) for two equivalent electrons,

TABLE I. *Relative intensities in the super-multiplet dp→ds, for (jj) coupling.*

ds– \ dp	4(1/2)			4(3/2)				6(1/2)		6(3/2)				Sums	
	j	2	1	3	2	1	0	3	2	4	3	2	1		
4(1/2)	2	5	5	14	5	1	0	0	0	0	0	0	0	30	
	1	5	1	0	5	5	2	0	0	0	0	0	0	18	48
6(1/2)	2	0	0	0	0	0	0	$7^7/_9$	$2^2/_9$	0	$6^2/_9$	$7^7/_9$	6	30	72
	3	0	0	0	0	0	0	$6^2/_9$	$7^7/_9$	18	$7^7/_9$	$2^2/_9$	0	42	
Sums		10	6	14	10	6	2	14	10	18	14	10	6		
		16		32				24		48					
		48						72							

TABLE II. *Relative intensities in the super-multiplet $(2p)^2$→2p3s for (jj) coupling.*

$(2p)^2$ \ 2p3s	4(1/2)			2(1/2)		Sums		
	j	1	2	1	0			
4(3/2)	0	2·2= 4	0	0	0	4	24	40
	2	2·5=10	2·5=10	0	0	20		
4(1/2)	2	5	5	0	0	10	16	
	1	1	5	0	0	6		
2(3/2)	2	0	0	10	0	10	16	20
	1	0	0	2	4	6		
2(1/2)	0	0	0	2·2=4	0	4	4	
Sums		20	20	16	4			
		40		20				

It is seen that the total intensity in a given system is proportional to the multiplicity of that system. For non-equivalent electrons both horizontal and vertical sums are proportional to the corresponding statistical weights, e.g. $^4(1/2):^4(3/2):^6(1/2):^6(3/2)=8:16:12:24$. For the equivalent electrons, the sums from the $(2p)^2$ states are likewise proportional to the statistical weights, e.g. $^4(3/2):^4(1/2):^2(3/2):^2(1/2)=12:8:8:2$.

However, this is not so for the sums from the 2p3s states, but would be true if the two p electrons were not equivalent. It should be noted that the $^4(1/2)$ and $^2(3/2)$ states of the $(2p)^2$ configuration have the same energy, but differ in the value of j which the valence electron has. (In the one case, $j_1=1/2$, $j_2=3/2$ and in the other case $j_1=3/2$, $j_2=1/2$ where j_1 denotes the

valence electron). The intensities given above for the transition $(2p)^2 \rightarrow 2p3s$ agree with those found from the general formulae of the previous paper,[2] when one sets the electrostatic interaction equal to zero.

As to the comparison with experiment, the observed intensities vary greatly from observer to observer, perhaps due to the excitation conditions. Furthermore, in some cases the identification of terms is in question. However, the intensities given by Mack[5] for the super-multiplet $d^9p \rightarrow d^9s$ in Ge V and SnV are not in any marked disagreement with what one should expect from Table I. Where (jj) coupling is not realized, it may sometimes be possible to interpolate between this case and that of (ls) coupling. This question, as well as the allied ones of term-crossing and co-ordination to series limits, is beyond the scope of the present paper, but in all probability can be treated by obtaining the general formulae for a few simple cases and by then applying the method of induction. The calculations involved are not impossibly complicated for two electrons.

In conclusion, I wish to thank Professor Slater for helpful suggestions, and Harvard University for the renewal of my Parker Travelling Fellowship.

[5] J. E. Mack, Phys. Rev. **34**, 17 (1929).

AN EXTENSION OF THE SPECTRUM OF Tl II

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Abstract

The spectrum of singly ionized thallium has been obtained by using the metal in a hollow cathode discharge in helium. Spectrograms have been made from 1900A. to 8000A. The newly found terms here reported are $6s8d\,^3D_{1,2,3}$, $6s8d\,^1D_2$, $6s9s\,^3S_1$, $6s10s\,^3S_1$, $6s6f\,^3F_{2,3,4}$, $6s7f\,^3F$ and an unclassified term $2_3{}^0$. Absolute term values have been calculated from the sequence $6s6d\,^3D_2$, $6s7d\,^3D_2$, $6s8d\,^3D_2$. The ionization potential is found to be 20.30 volts. Tables of term values and of about sixty newly classified lines are given. Fourteen new multiplets arising from the fine structure of the terms are also tabulated.

1. Introduction

THE spectrum of singly ionized thallium has been investigated by Rao, Narayan, and Rao,[1] by McLennan, McLay, and Crawford[2] and by Smith.[3,4] A further publication by McLennan, McLay and Crawford[5] has not only extended the number of known terms but has also revealed the fine structure character of some of the terms. A very interesting feature of the fine structure of the Tl II terms was found to be the relatively large values of the differences between the term components as compared with those previously found by Back and Goudsmit[6] for Bi I and by Jackson[7] for Cs I. McLennan, McLay and Crawford were able to account for the observed structure of the Tl II lines by assuming that the nucleus has a spin of quantum number $\frac{1}{2}$, as Jackson had previously found to be the case for the nucleus of Cs I.

The further progress in the elucidation of the Tl II spectrum which is here reported, has been made by examining the spectrum obtained from a hollow cathode discharge in helium.

2. Experimental

As the Schüler lamp and the experimental details of its use have been previously described by Schüler,[8] Paschen[9] and Sawyer[10] it is not necessary to enter into any detailed account of the apparatus. There is, however,

[1] K. R. Rao, A. L. Narayan, A. S. Rao, Indian Journ. Phys. **2,** 467 (1928).
[2] J. C. McLennan, A. B. McLay, M. F. Crawford, Trans. Roy. Soc. Can. **22,** 241 (1928).
[3] S. Smith, Proc. Nat. Acad. Sci. **14,** 951 (1928).
[4] S. Smith, Phys. Rev. **34,** 393 (1929).
[5] J. C. McLennan, A. B. McLay, M. F. Crawford, Proc. Roy. Soc. **A125,** 570 (1929).
[6] E. Back and S. Goudsmit, Zeits f. Physik **43,** 321 (1927) and **47,** 174 (1928).
[7] D. A. Jackson, Proc. Roy. Soc. **A121,** 432 (1928).
[8] H. Schüler, Zeits. f. Physik **35,** 323 (1926).
[9] F. Paschen, Sitz. Preuss. Akad. Wiss. **32,** 536 (1928).
[10] R. A. Sawyer and F. Paschen, Ann. d. Physik **84,** 1 (1927).

one point which is perhaps worthy of note. Due to the great rapidity with which thallium oxidizes it was found necessary to do most of the cleaning up of the Schüler tube by the usual device of passing a heavy discharge between the electrodes in oxygen before the thallium was introduced into the tube. The inner electrode, a hollow carbon cylinder closed at one end, was then removed and filled with molten thallium. A semi-circular hole was made

TABLE I. *Term values of Tl II.*

Term–	Value	Term intervals lower J first		
$6s^2\ {}^1S_0$	164600	$6s6p\ {}^3P^0$	2941	9333
$6s6p\ {}^3P_0{}^0$	115148	$6s7p\ {}^3P^0$	215	2456
$6s6p\ {}^3P_1{}^0$	112207	$6s6d\ {}^3D$	284	393
$6s6p\ {}^3P_2{}^0$	102874	$6s7d\ {}^3D$	127	149
$6s6p\ {}^1P_1{}^0$	88938	$6s8d\ {}^3D$	51	95
$6s7s\ {}^3S_1$	59374	$6s5f\ {}^3F^0$	−103	117
$6s7s\ {}^1S_0$	56603	$6s6f\ {}^3F^0$	10	−35
$6s6d\ {}^1D_2$	49436			
$6s6d\ {}^3D_1$	48448		Fine Structure Intervals*	
$6s6d\ {}^3D_2$	48164	Term	$\Delta\nu$	
$6s6d\ {}^3D_3$	47771	†$6s6p\ {}^3P_2{}^0$	3.5	
$6p^2\ {}^3P_0$	47191	†$6s7p\ {}^3P_1{}^0$	4.0	
$6s7p\ {}^3P_0{}^0$	45239	†$6s7p\ {}^3P_2{}^0$	3.5	
$6s7p\ {}^3P_1{}^0$	45023	†$6s6p\ {}^1P_1{}^0$	−.05	
$6s7p\ {}^3P_2{}^0$	42569	†$6s7p\ {}^1P_1{}^0$	−0.5	
$1_1{}^0$	42219	†$6s6d\ {}^3D_1$	−1.5	
$6p^2\ {}^3P_1$	39260	†$6s6d\ {}^3D_2$	1.0	
$6s7p\ {}^1P_1{}^0$	38394	†$6s7d\ {}^3D_1$	−2.5	
$6p^2\ {}^1D_2$	35781	†$6s7d\ {}^3D_2$	0.5	
$6s5f\ {}^3F_3{}^0$	28481	†$6s7d\ {}^3D_3$	4.0	
$6s5f\ {}^3F_2{}^0$	28378	$6s8d\ {}^3D_1$	−2.0	
$6s5f\ {}^3F_4{}^0$	28364	$6s8d\ {}^3D_2$	1.0	
$6s5f\ {}^1F_3{}^0$	28331	†$6s6d\ {}^1D_2$	2.0	
$6s7d\ {}^1D_2$	27707	†$6s7d\ {}^1D_2$	0.5	
$6s7d\ {}^3D_1$	26672	$6s8d\ {}^1D_2$	−5.0	
$6s7d\ {}^3D_2$	26545	†$6s7s\ {}^3S_1$	5.0	
$6s7d\ {}^3D_3$	26396	$6s9s\ {}^3S_1$	4.5	
$2_3{}^0$	21815	$6s5f\ {}^3F_2{}^0$	−2.0	
$6s9s\ {}^3S_1$	19185	$6s5f\ {}^3F_3{}^0$	1.0	
$6s8d\ {}^1D_2$	18182	$6s6f\ {}^3F_2{}^0$	−2.0	
$6s6f\ {}^3F_4{}^0$	18096	$6s6f\ {}^3F_3{}^0$	−2.5	
$6s6f\ {}^3F_2{}^0$	18071	†$1_1{}^0$	−0.5	
$6s6f\ {}^3F_3{}^0$	18061			
$6s8d\ {}^3D_1$	16997			
$6s8d\ {}^3D_2$	16946			
$6s8d\ {}^3D_3$	16851			
$6s10s\ {}^3S_1$	12852			
$6s7f\ {}^3F$	12484			

* A negative sign indicates that the component with smaller F value has the smaller term value.

† Given by McLennan, McLay and Crawford.[5]

in the carbon at the closed end and a semi-circular carbon stop was inserted in the open end to correspond with the remaining piece of carbon at the other end, so that when the electrode was put into the tube with its axis horizontal and the thallium was melted, the carbon acted as a trough to hold some of the molten metal. On replacing the electrode the cleaning process with the oxygen discharge was continued, care being taken to prevent the thallium from melting. The tube was then pumped out to a hard vacuum and the

helium made to circulate through the apparatus. A heavy discharge was then passed through the tube until the thallium became molten, when half the metal ran out on to the outside aluminum electrode leaving the carbon cylinder half full of thallium with an untarnished surface.

A potential difference of about 1500 volts was applied to the electrodes by means of a variable voltage transformer in series with a rectifying valve. The spectrum from 1900A to 8000A was photographed by means of a two meter grating arranged on a Rowland mounting and giving a dispersion of about 8.5A per mm in the first order. A Hilger interchangeable spectrograph was also used with quartz and glass trains. Neither of these instruments, although the best at the disposal of the writer, gives sufficiently large dispersion or high resolution for an accurate investigation of the fine structure. Consequently the fine structure separations measured are, at the best, only accurate to about one-half of a unit of wave-number.

3. Results

The newly found terms are $6s8d\,^3D_{1,2,3}$, $6s8d\,^1D_2$, $6s9s\,^3S_1$, $6s6f\,^3F_{2,3,4}$, $6s7f\,^3F$, an unclassified term here denoted by $2_3{}^0$ and $6s10s\,^3S_1$. The last mentioned term is given tentatively as only the $6s7p\,^3P_{0,1,2}$–$6s10s\,^3S_1$ combinations have as yet been found.

The term values given in Table I are arrived at by taking $6s^2\,^1S_0$ to be 164,600, a value which makes the Rydberg denominators of the three $6snd\,^3D_2$ terms vary in much the same way as do the corresponding terms of Hg I. The ionization potential of singly ionized thallium would then appear to be 20.30 volts.

The tabulated term values in the case of terms for which the fine structure differences have been measured are the averages of the term values of the two components, the fine structure intervals being listed on the right hand side of the table. To make the table as complete as possible all the previously found terms and fine structure intervals are also included.

Reference might be made to the abnormal nature of the $6s6f\,^3F$ terms. It will be noticed that the partial inversion of the terms differs from that of the $6s5f\,^3F$ terms Written in the order of descending magnitude the 5 F terms are F_3, F_2, F_4 while for the $6F$ terms the order is F_4, F_2, F_3. The unclassified term $2_3{}^0$ has a value very close to the estimated value of the $6s8p\,^3P_2$ term, but the intensity relations observed for its combinations with $6s6d\,^3D_{2,3}$ suggest that the inner quantum number is 3 and not 2. Moreover if $2_3{}^0$ were identified as $6s8p\,^3P_2$ a strong combination with $6s7s\,^3S_1$ would be expected at ν 37559. There is, indeed, a line of intensity 0 at λ2661.74 or ν 37558.3 but it is difficult to believe this could actually be $6s7s\,^3S_1$–$6s8s\,^3P_2$.

Table II contains the newly classified lines of Tl II and Table III shows in detail the new fine structure multiplets which have as yet been observed.

I wish to express my thanks to Dr. R. A. Sawyer through whose courtesy the essential parts of the Schüler lamp apparatus were made in the Department of Physics at the University of Michigan. My thanks are also due to

TABLE II. *New classified lines of Tl II.*

λ I A air	ν	Int.	Classification
5642.75	17717.0	4	$6p6p\,^1D_2-6s6f\,^3F_3^0$
4946.67	20210.0	3	~~$6p7p\,^1P_1^0-6s8d\,^1D_2$~~
4945.55	20214.6	2	
4660.99	21488.7	3	$6s7p\,^1P_1^0-6s8d\,^3D_2$
§4340.43	23032.7	1	$1_1^0-6s9s\,^3S_1$
4339.65	23036.9	1	
4292.4	23290.5	1	$6p^2\,^1D_2-6s7f\,^3F^0$
4291.5	23295.3	2	
4274.96	23385.5	10	$6s7p\,^3P_2^0-6s9s\,^3S_1$
4274.20	23389.6	2	
3955.94	25271.3	1	$1_1^0-6s8d\,^3D_2$
3955.45	25274.4	3	
3910.05	25567.9	1	
3909.49	25571.6	0	$6s7p\,^3P_2^0-6s8d\,^3D_1$
3909.15	25573.8	1	
3901.72	25622.5	9D	$6s7p\,^3P_2^0-6s8d\,^3D_2$
*3887.24	25717.9	?	$6s7p\,^3P_2^0-6s8d\,^3D_3$
3869.81	25833.8	2	
3869.19	25837.9	5	$6s7p\,^3P_1^0-6s9s\,^3S_1$
3868.59	25841.9	2	
3852.10	25952.5	3	
3851.67	25955.4	2	$6s6d\,^3D_3-2_3^0$
3837.49	26051.3	2	
3836.81	26056.0	4	$6s7p\,^3P_0^0-6s9s\,^3S_1$
3794.08	26349.4	10D	$6s6d\,^3D_2-2_3^0$
3724.79	26839.5	0	$6s7p\,^3P_1-6s8d\,^1D_2$
3619.43	27620.8	2	$6s6d\,^1D_2-2_3^0$
3567.56	28022.4	3	
3567.21	28025.1	0	$6s7p\,^3P_1^0-6s8d\,^3D_1$
3567.06	28026.3	0	
3566.75	28028.8	2	
3560.77	28075.8	5	$6s7p\,^3P_1^0-6s8d\,^3D_2$
3560.40	28078.7	4	
3540.05	28240.1	3	$6s7p\,^3P_0^0-6s8d\,^3D_1$
3539.78	28242.3	2	
3369.13	29672.8	10	$6s6d\,^3D_3-6s6f\,^3F_4^0$
3365.43	29705.4	1	$6s6d\,^3D_3-6s6f\,^3F_3^0$
3364.12	29717.0	2	~~$6s7p\,^3P_2^0-6s10s\,^3S_1$~~
3322.30	30091.0	2	$6s6d\,^3D_2-6s6f\,^3F_2^0$
3321.94	30094.3	1	
3321.17	30101.2	4	$6s6d\,^3D_2-6s6f\,^3F_3^0$
3320.80	30104.6	3	
3291.09	30376.4	6	$6s6d\,^3D_1-6s6f\,^3F_2^0$
3186.60	31372.4	2	$6s6d\,^1D_2-6s6f\,^3F_3^0$
3186.26	31375.7	1	
3107.73	32168.5	0	$6s7p\,^3P_1^0-6s10s\,^3S_1$
3086.53	32389.5	00	$6s7p\,^3P_0^0-6s10s\,^3S_1$
2833.27	35284.6	6	$6s6d\,^3D_3-6s7f\,^3F^0$
2801.85	35680.2	5	$6s6d\,^3D_2-6s7f\,^3F^0$
2780.25	35957.4	3	$6s6d\,^3D_1-6s7f\,^3F^0$
2705.55	36950.1	3D	$6s6d\,^1D_2-6s7f\,^3F^0$
λ I A vac			
†1413.12	70765	2	$6s6p\,^1P_1^0-6s8d\,^1D_2$
1310.22	76323	1	$6s6p\,^3P_2^0-6s7d\,^3D_2$
1169.07	85538	0	$6s6p\,^3P_1^0-6s7d\,^3D_1$
1162.56	86017	1	$6s6p\,^3P_2^0-6s8d\,^3D_3$
1018.81	98153	00	$6s6p\,^3P_0^0-6s8d\,^3D_1$
817.11	122382	8	$6s^2\,^1S_0-1_1^0$
792.29	126216	5	$6s^2\,^1S_0-6s7p\,^1P_1^0$

§ This line may be $H\gamma$.

* This line falls in the region of halation caused by the helium line λ3888.64: its intensity is therefore difficult to estimate.

† This line is attributed to Tl IV by Rao[11], but not by Mack.[12]

[11] K. R. Rao, Phys. Soc. London Proc. **41**, 361 (1929).

[12] J. E. Mack. Phys. Rev. **34**, 17 (1929).

TABLE III. *Fine structure multiplets of Tl II.*

	F	$6s7p\,^3P^0_0$	$6s7p\,^3P^0_1$		$6s7p\,^3P^0_2$	
		$\frac{1}{2}$	$\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$
$6s9s\,^3S_1$	$\frac{1}{2}$	26051.3 (2)	25837.9 (5)	25833.8 (2)	23385.5 (10)	
	$1\frac{1}{2}$	26056.0 (4)	25841.9 (2)	25837.9 (5)	23389.6 (2)	23385.5 (10)

	F	$6s7p\,^3P^0_0$	$6s7p\,^3P^0_1$		$6s7p\,^3P^0_2$	
		$\frac{1}{2}$	$\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$
$6s8d\,^3D_1$	$\frac{1}{2}$	28242.3 (2)	28028.3 (2)	28025.1 (0)	25573.8 (1)	
	$1\frac{1}{2}$	28240.1 (3)	28026.3 (0)	28022.4 (3)	25571.6 (0)	25567.9 (1)

	F	$6s7p\,^3P_1{}^0$		$1_1{}^0$	
		$\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$	$1\frac{1}{2}$
$6s8d\,^3D_2$	$1\frac{1}{2}$	28078.7 (4)		25271.3 (1)	
	$2\frac{1}{2}$		28075.8 (5)		25274.4 (3)

	F	$6s6d\,^1D_2$		$6s6d\,^3D_2$	
		$1\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$
$6s6f\,^3F_3{}^0$	$2\frac{1}{2}$	31375.7 (1)		30104.6 (3)	
	$3\frac{1}{2}$		31372.4 (2)		30101.2 (4)

	F	$6s7p\,^1P_1{}^0$			F	$6p^2\,{}^1D_2$	
		$\frac{1}{2}$	$1\frac{1}{2}$			$1\frac{1}{2}$	$2\frac{1}{2}$
$6s8d\,^1D_2$	$1\frac{1}{2}$	20214.6 (2)		$6s7f\,^3F_3{}^0$	$2\frac{1}{2}$	23290.5 (1)	
	$2\frac{1}{2}$		20210.0. (3)		$3\frac{1}{2}$		23295.3 (2)

	F	$2_3{}^0$			$6s6d\,^3D_2$	
		$2\frac{1}{2}$	$3\frac{1}{2}$		$1\frac{1}{2}$	$2\frac{1}{2}$
$6s6d\,^3D_3$	$2\frac{1}{2}$	25955.4 (2)		$1\frac{1}{2}$	30094.3 (1)	
	$3\frac{1}{2}$		25952.5 (3)	$6s6f\,^3F_2{}^0$ $2\frac{1}{2}$		30091.0 (2)

Dr. R. J. Lang for his advice in the assembling of the apparatus and in putting it into operation.

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IONIZATION IN THE UPPER ATMOSPHERE VARIATION WITH LONGITUDE*

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Abstract

Continuing a former paper (Phys. Rev. **34,** 1167 (1929)) the present paper gives theoretical calculations of the changes in the ionization in the upper atmosphere with longitude. The electrical conductivity of the upper atmosphere is about 1.4×10^{-5} at noon equinox at the equator and an order of magnitude less at night. The maximum density of electrons y_m varies with the latitude θ and longitude ψ, measured from noon equinox at the equator according to $y_m=3.14\times 10^5\cos\theta(0.18\sin\psi+\cos\psi)$ for the daylight hours. At night the expression is more complex. The values of y_m yield skip distances of short wireless waves roughly in accord with observation in the day but somewhat too great at night. The theory puts the shortest skip distance at 40 minutes past noon and observation in temperate zones gives 2 p.m.; the agreement is good, but not perfect.

IN A recent paper [11] the ionization in the upper atmosphere was worked out over the entire earth. The ionization, assumed to be caused by the ultraviolet light of the sun, was shown to explain certain facts of wireless wave propagation and of terrestrial magnetism. The variation of the ionization with latitude was described in some detail, less space being given to the variation with longitude. This paper presents the longitude calculations, and is therefore a direct continuation of the earlier paper, the nomenclature, numbering of paragraphs, equations, figures, tables and references being carried on from that paper.

33. It is assumed that the temperatures of the upper atmosphere for longitudes along the equator are given by the values of T of column 2, Table I, the degrees of latitude of column 1 being now degrees of longitude measured from high noon. For example, at 60° longitude, i.e., at 8 a.m. or 4. p.m. T is 360°K. At any point in the day hemisphere of longitude ψ and latitude θ the angular distance ζ from equatorial noon is $\cos\zeta=\cos\theta\cos\psi$ and $T=220+280\cos\zeta$. Everywhere in the night hemisphere T is 220°K. From the values of T the ionic recombination coefficient α is known at all points. The critical level z_c is nearly independent of the longitude; for example, at the equator z_c descends from the noon value of 150 km to 147 km at night, and the diurnal change at high latitudes is less.

34. In the S region the y, z curves for various longitudes were calculated for the daylight hours by the method of sections 10 and 11. The method neglected gravity diffusion of the ions and assumed that equilibrium existed between the rate of production and the rate of loss as expressed by

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[11] Hulburt, Phys. Rev. **34,** 1167 (1929).

$$q \cos \psi - \alpha n y^2 = 0. \tag{19}$$

The curves for the equator are given in Fig. 4. ("Gravity diffusion" is a short expression for "temperature diffusion of the ions to attain gravitational

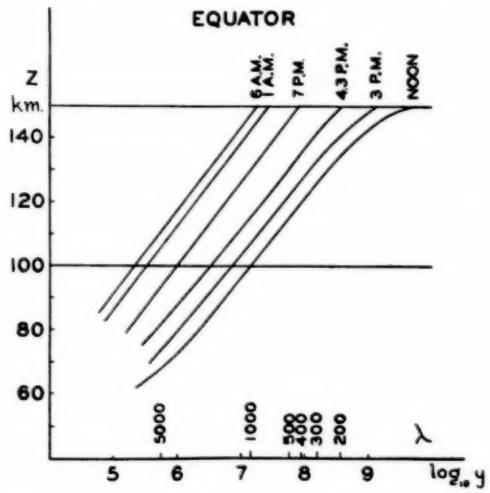

Fig. 4. Theoretical values of the density y of ion pairs in the S region of the upper atmosphere at the equator.

equilibrium.") Apart from the neglect of gravity diffusion (19) is an approximation because as the earth turns under the sun equilibrium in general does not exist. The more complete expression is

$$dy/dt = q \cos \omega t - \alpha n y^2, \tag{20}$$

where t is the time measured from high noon and ω is the angular velocity of rotation of the earth on its axis; $\omega = 7.28 \times 10^{-5}$ radians sec^{-1}. α and q are functions of the longitude ωt. Even if α and q are assumed to be constant with respect to t we are unable to solve (20) and must turn to approximate methods.

At noon at the equator $y = 5 \times 10^9$ for $z = 150$ km. At 1 p.m. y is 4.8×10^9 from (19). If there were no production of ions after 12 o'clock and the ions at 1 p.m. were those of noon decreased by recombination, y at 1 p.m. would be 1.5×10^9, as found from (20) with $q = 0$. Since this is less than one third the value of y (19) we see that the ions at 1 p.m. are mainly those formed by the sunlight at 1. p.m. rather than those left over from noon. Therefore, the maximum value of y at $z = 150$ km is reached within less than 20 minutes after noon. Similarly, it is found that the maximum of the ionization occurs later as z becomes less until at $z = 100$ km the maximum is near 1 o'clock. Thus, except for the small shift in the maximum, (19) gives values of y which are approximately correct during the day until about 4 p.m. After 4 p.m. (19) gives values of y which are too low; for example, it would make $y = 0$ at 6 p.m., whereas at this hour many of the ions formed during the day still exist, and indeed continue to do so all night. From (19) and from (20) with $q = 0$ it comes out that at about 4.7 p.m. the number of ions in equilibrium with the

ultra-violet radiation is equal to the number left over from the earlier hours. We therefore calculate the y, z curve for 4.3 p.m. by means of (19), assume no more production of ions and calculate the y, z curves for various hours through the night from (20), with $q=0$. The night-time y, z curves for the equator are given in Fig. 4. In like manner the y, z curves throughout day and night were determined for all latitudes. The curves of Fig. 4 are probably not plotted entirely correctly, those at night being lifted up too much. Due to the cooling and contraction of the atmosphere at night and at the higher latitudes, mentioned in sections 17 and 19, the upper atmosphere is lower than at equatorial noon. The decrease in height from noon to midnight is about 25 and 15 km at 140 and 100 km, respectively. This would bring the night y, z curves closer to the noon curve than are shown in Fig. 4.

35. The height z at which a wireless wave of wave-length λ is totally reflected (refracted) at normal incidence is found by putting the refractive index μ equal to zero in the expression $\mu^2=1-2ye^2\lambda^2/\pi m$, solving for y and determining z from the y, z curve. The values of y for total reflection of waves of length 5,000, 1,000, 500, 400, 300, and 200 m are marked along the X-axis of Fig. 4. It is seen, for example, that the height reached by 1,000 m waves increases on the equator from 100 km at noon to 140 km at midnight and to 150 km in the early morning before dawn, with similar increases in the heights reached by the other long waves. The heights for total reflection at latitudes 40°, 60°, and 70° are, respectively, 5, 12, and 19 km greater than the corresponding heights at the equator. But due to the shrinkage of the atmosphere at night and at the higher latitudes the increase in the height is probably less. On the whole the heights reached by the longer waves change but little with the latitude and the time of day. This is in accord with the facts as far as they are known. It must be remembered that the observation of the height reached by wireless waves gives always an "apparent height" which is in general greater than the true height. This is due to the group velocity retardation of the wave in the ionized region of the atmosphere. Therefore, the interpretation of a height measurement is always open to some uncertainty and, in the case of the echo experiments, is often ambiguous for it is sometimes difficult to know where the echo has come from.

36. The absorption of wireless waves calculated from the y, z curves showed that in the region below the height of total reflection the intensity of 500 m waves, for example, was reduced to $1/\epsilon$'th by passage through 20, 25 and 80 km of the medium at noon at latitudes 0°, 40° and 60° respectively. These values are, if anything, below those inferred from qualitative observation. A suitable number of electrons which undoubtedly exist in this region may be called upon to give the correct absorption. The absorption of 5,000 m waves is greater than is observed if the y, z curve is assumed to continue according to the arbitrary formula of section 10 below the height where these long waves are reflected. We may conclude, as is quite reasonable, that y becomes small and that the formula is not valid in the levels below 70 km at equatorial noon.

For 500 m waves the absorption at 4 p.m., 7 p.m. and midnight was about 0.3, 0.07 and 0.01 of the noon values. The absorption thus decreases fairly rapidly at sunset, but perhaps not quite rapidly enough. It is well known that the intensity of broad-cast waves received at some distance increases rather sharply at sunset, passing within less than two hours from its low daylight value to a high night value. Although the observations are only qualitative it would seem that they might call for a more pronounced change at sunset than the y, z ion curves can give. Electrons in the S region will disappear rapidly after sunset and may account for the sharp change in the wireless phenomena. Since 1 electron is equivalent to about 10^6 ions as far as absorption is concerned and to 10^5 ions for refraction purposes, it is possible to have the absorption in the daylight S region controlled by electrons and the refraction by ions.

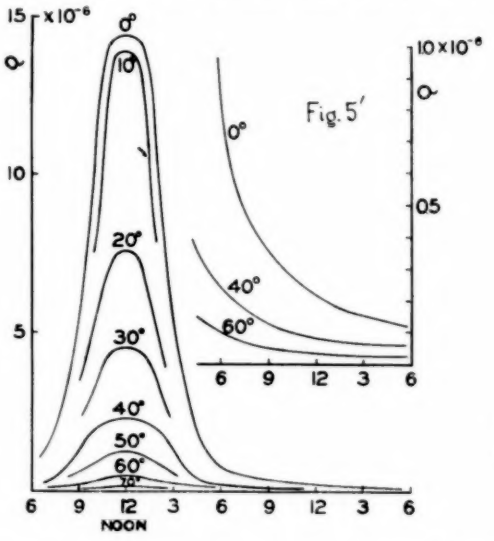

Fig. 5. Theoretical values of the electrical conductivity σ of the upper atmosphere.

In this connection an interesting difficulty appears. Experiments with long waves indicate that the polarization of the received wave varies more or less rapidly with the time during the day and the night. The explanation usually given is that the upper atmosphere contains electrons which are influenced by the earth's magnetic field and cause magnetic double refraction and absorption of the wave. Ions are too heavy to give rise to appreciable double refraction except for very long waves beyond the normal wireless range. Electrons produced by the ultra-violet light of the sun, in all probability, exist in the levels below 150 km during the day, but one would expect them to disappear very rapidly at night. For example, the rate of decrease of the electron density y_e due to attachment of the electrons to oxygen molecules of density n' is $dy_e/dt = -bn'y_e$ where $b = 7 \times 10^{-14}$. At 120 km at night $n' = 1.72 \times 10^{11}$. Thus $\log_e y_e/y_0 = -0.012t$ and in 10^3 seconds or 17 minutes y_e becomes very small. The decrease is greater at the lower heights. The diffusion of electrons down from higher levels is inappreciable. Therefore, if the observations de-

mand electrons in the 70 to 140 km levels at night we shall conclude that something has been left out of the present theory. It is possible that the interference of a number of rays may give rise to changes in the polarization of the received wave quite apart from magnetic double refraction effects.

37. From the y, z curves the values of the electrical conductivity σ of the S region were calculated by means of (12) and were plotted in Fig. 5 for various longitudes and latitudes. In Fig. 5′ the night values of σ are given on a larger scale. Summing up the values of σ over the light and dark hemispheres gives the ratio of the total night to day conductivity to be 1/20; this value was used in section 18. The electrical conductivity of copper is 5.9×10^{-4} and of mercury is 1.06×10^{-5} c.g.s.e.m. u. The conductivity of a 1 cm^2 column vertically upward through the S region of the atmosphere is about 1.4×10^{-5} at equatorial noon and 10^{-6} at sunset, and is therefore equivalent in these two cases to that of 14 and 1 mm of mercury, respectively.

38. Concerning the variation of the D ions with longitude there is little to add to what has already been said in sections 13 to 16. The calculations of the D ions were on the whole pretty rough because so many simplifying assumptions were made. To improve the calculations appears to be intricate and the mathematical difficulties promise to be appreciable. At equatorial noon the magnetic susceptibility of each cm^3 of the D region is about two orders of magnitude greater than that of bismuth, bismuth being the most strongly diamagnetic substance known.

39. The electrons were shown[1] to attain their maximum density y_m at a height of 190 km at summer noon. The y_e, z curve for noon at $\theta=17°$ (as at Washington, D. C., on June 22) is given in curve 1, Fig. 2, reference 1, in which $y_m=3\times10^5$. We use this curve and adopt the simplifying assumption (reference 1, page 1029) that during changes in the curve, which occur during the day and night, the electron density y_e at each point on the curve changes in the same proportion. This enables all the calculations of the y_e, z curve to be reduced to a calculation of the changes in y_m. The physical justification for this assumption lay in the fact that most of the electrons were produced somewhere above the maximum and diffused rapidly downward to build up their maximum density approximately at a height where the loss due to attachment to oxygen molecules became greater than the supply due to diffusion from above, the loss increasing and the rate of diffusion decreasing as z became less. Therefore, if the rate of production q grew less y_e diminished at all points of the curve, and the assumption is that y_e diminishes equally at all points of the curve. Using the calculations of reference 1, page 1030, and changing them to refer to the somewhat higher day temperatures of the present paper, the total loss sec^{-1} of electrons above y_m due to attachment is 1.59×10^8 or $530y_m$. The loss due to the recombination of electrons with positive ions is negligible; this is fortunate, for the recombination term involves a y_m^2 which would make the equation hard to solve. The loss due to the electrical drift downward during the day with velocity v is 250 y_m, using an average value $v=250$ cm sec^{-1} among the values of v of column 9, Table I. The loss due to gravity diffusion across the maximum is 166 y_m, but this we leave

out. For gravity diffusion can not occur in its full extent simultaneously with the electrical drift as it involves molecular collisions which interfere with the drift. Therefore the rate of loss is approximately $(530+250)\ y_m=780y_m$.

The total number of electrons above the maximum is $5.76\times10^{11}=1.95y_m$. The rate of production is $q\cos\theta\cos\omega t$ where q is the rate at equatorial noon equinox, i.e., the sun directly overhead. Then

$$dy_m/dt=q\cos\theta\cos\omega t-780y_m/1.95\times10^6. \tag{21}$$

Solving

$$y_m=\frac{q\cos\theta}{16\times10^{-8}+\omega^2}(\omega\sin\omega t+4\times10^{-4}\cos\omega t). \tag{22}$$

Putting $t=0$, $y_m=3\times10^5$, $\theta=17°$ and $\omega=7.28\times10^{-5}$ in (22) gives $q=130$, and (22) becomes

$$y_m=3.14\times10^5\cos\theta(0.18\sin\omega t+\cos\omega t). \tag{23}$$

With this expression the values of y_m were calculated over the daylight hemisphere and are plotted in the full line curves of Fig. 6. The maximum value of y_m occurs at about 40 minutes past noon. Formula (23) is not valid at night for the sunset to sunrise voltage E reverses in sign at sunset and hence the downward daytime electrical drift velocity v changes after sunset to an up-

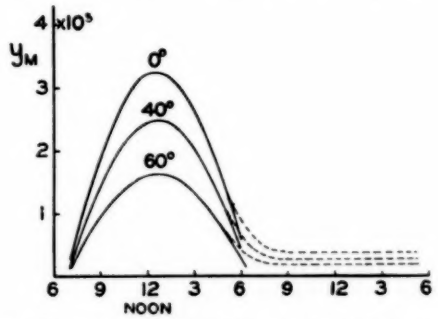

Fig. 6. Theoretical values of the maximum electron density y_m in the upper atmosphere.

ward velocity. At night (18) is used. (23) gives too low values of y_m as sunset is neared, for at this time the rate of loss of the electrons grows less because the downward electrical drift diminishes due to the decreasing E and the attachment coefficient diminishes due to the cooling temperature. Therefore the night curves, calculated from (18) and plotted in the dotted lines of Fig. 6 were joined to the day curves at 5 p.m.

40. The skip distance $2s$ for a wireless wave of length λ is given approximately by

$$2s=2h(\pi m/y_m e^2\lambda^2-1)^{1/2}, \tag{24}$$

where e and m are the electronic mass and charge, respectively, and h is the value of z for y_m. h was taken to be 190 km with the sun directly overhead, to be 140 km along the sunset and sunrise longitudes and to vary between these limits over the day hemisphere according to $\cos\theta\cos\omega t$. During the night the electrons move upward with a velocity roughly 250 cm sec^{-1} or 9 km hr^{-1}. Therefore h increases 9 km each hour during the night being 140 km at night-

fall and 210 km 8 hours later. With these values of h and with y_m from the curves of Fig. 6, the values of $2s$ for $\lambda 32$ meters were calculated from (24) and are plotted in Fig. 7. The skip distances for other short wireless waves calculated from (24) are approximately proportional to those for $\lambda 32$ meters. During the day the skip distance of Fig. 7 agree within 50 percent with the observed values as far as they are known; in the small hours of the night the calculated values appear to be on the whole 1.5 to 2 times too great.

Equation (24) is not exact for it leaves out of account the magnetic field and the curvature of the earth; the neglect of the first gives too long and of the second too short skip distances, the error due to the approximations being in general less than 30 percent. (24) also assumes sharp reflection of the wave at a height h and therefore neglects refraction by ions and electrons below y_m. The inclusion of this refraction will lessen the calculated skip distances. The

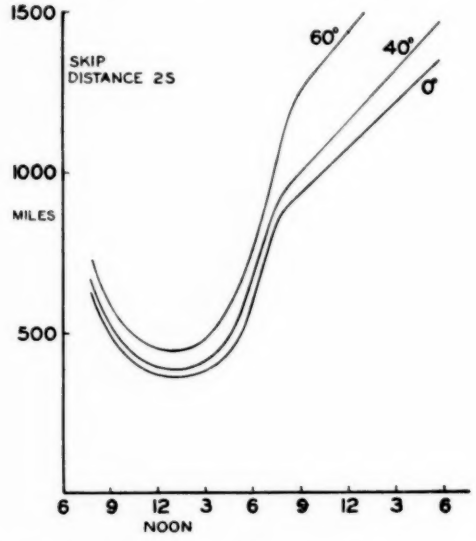

Fig. 7. Calculated values of the skip distance $2s$ for a 32 meter wireless wave.

skip distances of Fig. 7 are a minimum at 40 minutes past noon, the time when y_m is a maximum. Observation in temperate latitudes puts the shortest skip distance at about 2 o'clock. The agreement between theory and experiment is therefore good but not perfect. It is difficult to give a satisfactory explanation of the slight discrepancy; perhaps the value of the attachment coefficient is a little high, or perhaps there are shifts in the distribution of the ionization below the maximum which cause a warping of the ray paths.

41. In conclusion, it may be stated that an ionization produced by the ultra-violet light of the sun has been worked out which accounts in a general way for wireless wave propagation phenomena over the earth and for the part of the earth's magnetic field of external origin and its diurnal variations. We can not regard, however, the ionization which has been obtained as a unique solution of the problem of the ionization of the upper atmosphere. The ionization can be modified within limits in a number of ways without disturbing

the present conclusions, and probably some modification may be desirable for the numbers of ions and electrons which have been used may be slightly too great.

With the sun directly overhead D is 1.5×10^{16} atomic nitrogen ion pairs from 150 to 180 km, or the ion density is 10^{10}. From the relation[12]

$$\mu^2=1-ye^2\lambda^2/(1-He\lambda/2\pi cm)\pi m, \tag{25}$$

it is seen that 10^{10} atomic nitrogen ions give the same refraction for 40 meter waves as 3.2×10^5 electrons. Therefore at equatorial noon either the ions or the electrons will account for the wireless skip distances equally well, but both the 3.2×10^5 electrons and the 10^{10} ions are unnecessary, although to be sure there is no objection to having both if they are at different levels. Early in the morning and late in the afternoon the refraction of the ions falls below that of the electrons, as calculated from the values of y and y_e of the foregoing paragraphs, and at night it rises above the electronic refraction. If the observational facts of short wireless waves call for a refraction predominately electronic there are several ways in which the refractive effects of the ions may be decreased without disturbing the present development. One may keep the same number of ions and suppose that, say, one-half are molecular ions. This will decrease their refraction, change the drift currents and modify the calculations throughout, but will not change any of the values by as much as 100 percent. Or, one may decrease the number of ions and assume higher noon temperatures. In illustration, let us suppose that the number of ions were 1/2 and the noon temperatures 2 times the respective values which have been used. This will multiply the day values of σ and E by 1/4 and 3/2, respectively. The currents in the D and S regions for day and night, instead of being, respectively, about 11.6, 8.7, 2.3 and 0.6, become 6, 3, 2.5 and 0.5 millions of amperes. The steady current around the earth and the diamagnetism are unchanged.

On the other hand one can not be entirely certain that it is the ions which should be reduced. Actually the ions will give very closely the same skip distance-wave-length relation as the electrons. Therefore if the refraction of short wireless waves were due to ions rather than to electrons the skip distance theory[12] would be unchanged. In this case it would be an "ion limitation" theory rather than an "electron limitation" theory. A sufficient number of electrons could be assumed such that by their magnetic double refraction and absorption they would account for the dip in the wireless range curve at λ200 meters[12] and the polarization phenomena. It is doubtful whether at the present time the observational data permit a final decision among the various possibiliiies. We may express the view, based on the complexity of wireless wave behavior, that some complex modification may be the one which will best account for all of the facts. That is, that perhaps the ions and electrons are present in such numbers that their refractions are about equal, and that during certain hours of the day or night and at certain latitudes the refraction of wireless waves is controlled by electrons and at other times and latitudes by ions.

[12] Taylor and Hulburt, Phys. Rev. **27,** 189 (1926), equation 2.

THE SURFACE HEAT OF CHARGING

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Abstract

In recent papers by Bridgman, Langmuir and Tonks, and the author, the deviation of the constant A of *thermionic emission* from the theoretical value has been linked with the surface heat of charging and the *temperature variation of the photoelectric threshold*. In the present paper, at least a part of this effect is explained by the heat expansion of the material together with the dependency of the *work function* on the volume. Numerical calculations both for the deviations of A and for the temperature change of the threshold are made and compared with experiments. Before deciding whether the explanation given here is complete it will be necessary to calculate the space-charge effect of the electrons in the transition layer on the surface of the metal.

I. Introduction

THERE is considerable interest shown in the discussion of the formula for the thermionic emission, to which Richardson gave the form

$$i = BT^2 e^{-b/T}. \tag{1}$$

Equivalent to this, but better suited for our pupose, is the formula for the equilibrium density of the electron gas.

$$c = AT^{3/2} e^{-q/kT}. \tag{2}$$

in which A should be a universal constant[1,2]

$$A = (2\pi mk)^{3/2}/Nh^3. \tag{3}$$

Here the exponent $3/2$ of T comes about by putting the specific heat of the electron gas equal to $3R/2$, the specific heat of the electrons in the metal zero.[3]

Independent of this assumption, one can give general formulas connecting vapor pressure and heat of evaporation.[4,5,6] For example Lane[2] and Schottky[7] write in generalization of (2)

[1] O. W. Richardson, Proc. Cambr. Phil. Soc. **11,** 286 (1901); Phil. Mag. **28,** 633 (1919); Proc. Roy. Soc. **A91,** 530 (1915); Phys. Rev. **23,** 153 (1923).

[2] M. v. Laue, Jahrb. d. Rad. **15,** 205, 257 (1918); S. Dushman, Phys. Rev. **21,** 623 (1923). The same formula had been found by K. F. Herzfeld, Phys. Zeits. **14,** 1119 (1913) but he had made no applications of it.

[3] A. Sommerfeld Zeits. f. Phys. **47,** 1 (1928).

[4] O. W. Richardson, The Electron theory of Matter, Cambridge, 2 ed., 1916 p. 445.

[5] W. Rodebush, Phys. Rev. **23,** 774 (1924); H. A. Wilson, Phys. Rev. **23,** 38 (1924).

[6] C. Davisson and L. H. Germer, Phys. Rev. **20,** 300 (1922); **30,** 634 (1924).

[7] W. Schottky, Handb. d. Experimentalphysik, Vol. XIII, Leipzig 1928, p. 30.

$$c = AT^{3/2}e^{-\mu_s/kT} \tag{4}$$

where μ_s is the chemical potential of the electrons in the metal instead of their potential energy (in other words, the assumptions leading to (2) are equivalent to say $\mu_s = q$) and then proceeds to allow for μ for example a linear variation with T. This procedure is thermodynamically quite correct but leaves the question why μ is a linear function of T unanswered.

As a next step, one can introduce the specific surface heat of charging as the specific heat which enters into the thermodynamical equations.[6,8,9] It has been shown that such an effect might change the apparent value of A, the value of which agrees well experimentally with (3) in many cases but by no means always.

One can on the other hand consider the fact that the mutual potential energy which holds the electrons in the lattice will depend on the lattice distance and if heat expansion occurs will accordingly depend on the temperature.[10] This is closely connected with the temperature variation of the long-wave-length limit of the photoelectric effect. How to treat such a case has been discussed in a short paper[11] but no formulas have been given and some remarks there seem now incorrect.

Bridgman,[12] in a paper that appeared before the one last mentioned has shown quite clearly how the two effects of a variation of the photo-electric stopping potential with temperature and the surface heat of charging are connected and will modify A.

The present paper, while using a different scheme of thermodynamical calculations than Bridgman because it seems simpler, is intended to supplement it by showing just what values the surface heat of charging must have.

We propose first to give the calculations for a somewhat simplified case, in the second part we will discuss a few subtle points to justify our method of procedure.

II. Calculations for a Simplified Case

1. The free energy.

Consider a piece of metal, insulated and surrounded by vacuum. Call the number of electrons the metal contains in excess of the neutral state n, the free electrons in the vacuum n'. Let p be the pressure, V the volume of the metal, V_0 its normal volume when neutral and at zero pressure, $\Delta = (V - V_0)/V_0$.

We then write the formula for the free energy F of the whole system.

$$F = U(V) - nq(V) - \frac{1}{2}en\phi - T\Phi\left(\frac{h\nu}{kT}\right) - Tn\tilde{\Phi} + n'(\mu_G - kT).$$

[8] L. Tonks and I. Langmuir, Phys. Rev. **29,** 524 (1926); L. Tonks, Phys. Rev. **32,** 284 (1928).

[9] P. W. Bridgman, Phys, Rev. **27,** 143 (1926).

[10] O. W. Richardson, Phil. Mag. **23,** 594 (1912).

[11] K. F. Herzfeld, Sommerfeld Festschrift, Leipzig, 1928, p. 143.

[12] P. W. Bridgman, Phys. Rev. **31,** 90 (1928).

Here $U(V)$ is simply the (elastic) energy of the neutral metal. On account of deviations from neutrality, there is additional energy, an unelectric part[15] $-nq(V)$ and an electric part $(-1/2)en\phi$. In contradiction to Schottky[13] but in accord with Eckardt[14] we call electric only the part of the field due to excess charges and having accordingly a long range. This part can be changed by connecting the plate with outside sources. Accordingly $\phi=0$ means that there is no field of long range present. The energy then necessary to remove an electron is called the unelectric part $q(V)$. Φ is the integral

$$\Phi\left(\frac{h\nu}{kT}\right)=\int_0^T\frac{dT}{T^2}\int_0^T C_v dT \tag{5}$$

for the specific heat of the metal and will be usually a Debye function. Through ν, it will depend on the volume. We assume, (for the discussion of this assumption see under III) that ν does not depend explicitly on the charge.

$n\tilde{\Phi}$ would be the corresponding integral taken over the specific heat of the electrons in the usual sense, as calculated by Sommerfeld.[3] $\partial(n\tilde{\Phi})/\partial n$ corresponds to the part variable with temperature in Sommerfeld's expression of $2kT\ln A$ (which has as physical meaning just the electron part of our $\partial F/\partial n$) and is negligible up to 3000° ($2\cdot10^{-3}$ compared with 1, although it accounts for Thomson- and thermoelectric effects).

Finally, μ_G is the usual expression for the chemical potential of the electron gas

$$\mu_G=kT\ln c+(3/2)kT\ln T+kT\ln A\,. \tag{6}$$

2. Equilibrium formula.

In equilibrium, F will be a minimum in respect to the possible variations, namely of n(electron emission) and of volume. The first condition will give the equilibrium concentration, the second the equation of state of the charged metal (in making this latter variation, we neglect the fact that an increase of the volume of the metal will decrease the volume of the electron gas).

$$0=-\left(\frac{\partial F}{\partial n}\right)_v=q(V)+\frac{1}{2}e\phi+\frac{1}{2}en\frac{\partial\phi}{\partial n}+T\frac{\partial}{\partial n}(n\tilde{\Phi})+\mu_G \tag{7}$$

$$0=-p=\left(\frac{\partial F}{\partial V}\right)_n=\frac{\partial U}{\partial V}-n\frac{\partial q}{\partial V}-\frac{1}{2}en\frac{\partial\phi}{\partial V}-\frac{h}{k}\Phi'\frac{\partial\nu}{\partial V}-Tn\frac{\partial\tilde{\Phi}}{\partial V}\,. \tag{8}$$

As at least in first approximation $n\partial\phi/\partial n=\phi$ and as we have decided to neglect $\tilde{\Phi}$, we get from (7)

$$-\mu_G=q(V)+e\phi \tag{9}$$

[13] W. Schottky, Handb. d. Exp. Phys. Vol. XIII, 2 half p. 14 Leipzig 1928.

[14] C. Eckardt, Zeits. f. Physik **47**, 38 (1928).

[15] In this we include the part of the internal electron pressure effect which does not depend on temperature, namely $-W_i$ (Sommerfeld) so that $q=W_a-W_i$.

or

$$c = A T^{3/2} e^{-(q(V)+e\phi)/kT} \tag{10}$$

which for constant volume of the metal, is identical with the usual form (2).

The problem is then to find $q(V)$. Here we use the following approximations: As U refers to the neutral metal, we introduce the common compressibility κ and write, using a familiar development in powers of Δ

$$U(V) = U_0 + V_0 \Delta^2 / 2\kappa. \tag{11}$$

Furthermore, we assume

$$q(V) = q_1 - q_2 \Delta \tag{12}$$

with the expression

$$q_2 = -V_0 \partial q / \partial V.$$

This gives

$$\frac{\Delta}{\kappa} + \frac{n q_2}{V_0} - \frac{1}{2} e n \frac{\partial \phi}{\partial V} + \frac{h\nu}{k V_0} \Phi' \gamma = 0 \tag{13}$$

using Gruneisen's result,[15a] that

$$-\gamma = (V_0/\nu) \partial \nu / \partial V \tag{14}$$

is a constant, namely about 1-3 for many metals.

Using the expansion coefficient α for the uncharged metal ($n = 0$), which is according to Gruneisen given by

$$\int_0^T \alpha dT = -\kappa \frac{h\nu}{k V_0} \gamma \Phi' \tag{15}$$

we find

$$\Delta = \int_0^T \alpha dT - n q_2 \frac{\kappa}{V_0} + \frac{1}{2} e n \kappa \frac{\partial \phi}{\partial V}. \tag{16}$$

For the approximately neutral metal, $n = 0$, $\phi = 0$, we have

$$c = A T^{3/2} e^{-q_1/kT} \exp\left[\frac{-q_2}{kT} \int_0^T \alpha dT\right]. \tag{17}$$

The last factor is the deviation from the formula (2). It is simply the change in q due to the total expansion of the metal up to T.

Equation (17) can be written for sufficiently high temperature

$$c = A' T^{3/2} e^{-q_1/kT} \tag{18}$$

$$A' = A \exp\left[\frac{q_2}{kT} \int_0^T \alpha dT\right] = A e^{q_2 \alpha / k} \tag{19}$$

[15a] E. Gruneisen, Ann. d. Physik **39**, 257 (1912).

3. Calculation of q_2 and numerical value of A'.

It is possible to get an estimate of q_2. We have first to remember that q is a difference between the potential energy of an electron in the metal (Sommerfeld's W_a) and the effect of the internal pressure. (W_i according to Sommerfeld.) Therefore

$$-q_2 = V_0 \frac{\partial W_a}{\partial V} - V_0 \frac{\partial W_i}{\partial V}$$

Bethe[16] attempts a theoretical calculation of W_a; it is composed of a contribution from the positive ions, which is, for a given size of the ions, proportional to their numer per unit volume and which we call therefore

$$W_a^+ V_0 / V$$

and a contribution from the electrons, inversely proportional to the distance, or

$$W_a^- (V_0/V)^{1/3}.$$

Finally, W_i is proportional to the 2/3 power of the number of electrons per cm^3.

If we assume that compression does not change the total amount of electrons per atom, we have (W_a^+, W_a^-, W_i^0 constants)

$$q = W_a^+ \frac{V_0}{V} + W_a^- \left(\frac{V_0}{V}\right)^{1/3} - W_i^0 \left(\frac{V_0}{V}\right)^{2/3}. \tag{20}$$

Then

$$q_2 = W_a^+ + \tfrac{1}{3} W_a^- - \tfrac{2}{3} W_i^0. \tag{21}$$

According to Bethe's calculations for nickel, W_a^+ is about 13 volts, W^- 6 volts, W_i^0 15 volts, which would make $q_2 \sim 5$ volts.

If we write $\alpha = \alpha' \times 10^{-5}$, $q_2 = +q_2'$ volt, we have

$$e^{q_2 \alpha / k} = 10^{0.059 q_2' \alpha'} \tag{22}$$

From this it follows: A is always apparently increased $A' > A$. For $q_2' \alpha' < 10$ the factor multiplying the theoretical A is not larger than 3, which is within the limits of the experiment. If the above estimate of q_2 is correct, this means for metals with low expansion coefficient ($\alpha' < 2$), that the theoretical value of A can be made to fit the results.

But we have to expect much higher A's if α' is larger. $\alpha' = 9$ (linear expansion coefficient 3), $q_2' = 5$ means already $A' = A \cdot 10^{2.25} \sim 180 A$; $\alpha' = 15$, $q_2' = 6$ means $A' = 30.000\, A$.

While this is in the right order of magnitude, [18,19] we can give no reason why a large A' should always go with a high q_1.

[16] H. Bethe, Ann. d. Physik **87,** 55 (1928).

[17] The factor $\exp[-(1/k)\, \partial(n\tilde{\Phi})/\partial n]$ which is responsible for the thermoelectric effects has been neglected.

[18] C. Zwikker, Proc. Amst. Ac. **24,** 1 (1926); A. L. Du Bridge, Phys. Rev. **31,** 236 (1928); **32,** 961 (1928).

[19] A. L. Du Bridge, Proc. Nat. Ac. **14,** 788 (1928); I. Langmuir and K. H. Kingdon, Phys. Rev. **34,** 129 (1929).

4. Temperature change of the heat of evaporation.

We are first going to calculate the heat of evaporation of the electron and show that the deviation can be interpreted as a contribution of the specific surface heat of charging, not to C_v, but to $C_p - C_v$.

The heat of evaporation of an electron at constant volume of the metal would be

$$q(V) + 3RT/2 + e\phi \tag{23}$$

the middle part coming from the specific heat of the electron gas. The contribution of the specific heat of the electrons in the metal has been neglected.

At constant pressure, we have to add to (23)

$$T^2\left(\frac{\partial}{\partial V}\frac{\mu}{T}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{p,n}$$

or take simpler

$$T^2\left(\frac{\partial}{\partial T}\frac{\mu(p,T)}{T}\right)_{p,n} + \frac{3}{2}RT. \tag{24}$$

This is, with

$$\mu(p=0,T) = -q_1 - \frac{h\nu}{k}q_2\frac{\gamma}{V}\kappa\Phi' \tag{25}$$

from (7) for the uncharged plate, $n=0$, leads after a short calculation to the following formula in which the value of Φ has been introduced

$$q_1 - q_2\frac{\gamma}{V_0}\kappa\left(C_vT - \int_0^T C_v dT\right) + \frac{3}{2}RT. \tag{26}$$

Instead of the last $3RT/2$, $2RT$ or $5RT/2$ might have to be introduced, depending on which heat is actually measured.[6]

The interesting point is that for moderate temperatures, $C_vT - \int_0^T C_v dT$ is a constant or, in the presence of zeropoint energy in the vibrations of the solid, even zero. The exponent $-q_1/RT$ in (3) gives therefore at moderate temperatures the real heat of evaporation (apart from the member $3RT/2$, which is due to the electron gas).

In making this statement, we have again neglected the increase with temperature of the kinetic energy of the electrons in the metal as too small to detect. We can expect to find a change of the heat of evaporation with temperature:

(a) at high temperature, where C_v increases

$$C_v = C^0 + C'T$$

$$C_vT - \int_0^T C_v dT = \frac{C'}{2}T^2, \quad \Delta q = -q_2\frac{\gamma}{V_0}\kappa\frac{C'}{2}T^2.$$

This increase will not modify greatly the last factor in (17) because it occurs at high temperatures ($1/T$).

(b) at low temperatures, where quantum effects appear in the specific heat, there will be an increase in the heat of evaporation (apart from $3RT/2$) with decreasing temperature up to the amount

$$q_2\gamma\kappa N h\nu/V_0.$$

The value of the specific surface heat of charging at constant pressure follows from (26) to be

$$q_2\frac{\gamma k}{V_0}T\frac{\partial C_v}{\partial T}$$

(C_v specific heat of the metal at constant volume.) Bridgman[9,12] has shown that if (2) is valid and A' different from A, the specific surface heat of charging must be 0 and there must exist an entropy difference between the charged and the uncharged surface at zero temperature contrary to Nernst's heat theorem. In the case considered here the specific surface heat of charging is zero at zero temperature, takes then positive values and decreases to zero again for high temperatures. Accordingly (2) is valid at very low temperatures with the theoretical A, ceases to be valid afterwards and becomes valid again at high temperatures with $A'>A$. This hump of the specific heat at low temperatures is then responsible for the deviation of A' from A. If one would exterpolate formula (2) with A' different from the theoretical value to zero temperature one would find an entropy difference. A very similar situation is present in a number of chemical reactions. The whole situation is bound up with the fact that the expansion coefficient disappears at zero temperature which fact itself is again connected with Nernst's theorem.

Numerical calculations for the case of potassium give the following result: We use

$$\gamma=1.34^{20}\quad \kappa^{21}=35.6\times10^{-12}\quad V_0=45\quad h\nu/k=99^{22}$$

and for $C_v-(1/T)\int_0^T C_v dT$ tables given by Simon.[23]

If we take $q_2=5$ volt we find

T	$\beta\nu/T$	$CT-\int CdT$ (cal/Mol)	Δq(millivolts)
495	0.2	0	0
198	0.5	8	1.7
99	1	36	7.8
49	2	92	20
20	5	170	37
10	10	196	43

[20] E. Grüneisen, Handb. d. Phys. X p. 29, Berlin 1926.
[21] Reference 20, p. 38.
[22] A. Eucken, Handb. d. Exp. VIII, Leipzig 1929, p. 245.
[23] F. Simon, Handb. d. Physik X Berlin, 1926.

5. Photoelectric threshold.

Offhand, one could be doubtful whether the photoelectric threshold is determined by the energy or the free energy of the electrons in the metal. But Bridgman has proved the connections between threshold and contact potentials, and there is no doubt that the contact potentials are determined by the free energy or, more exactly, the chemical potential μ.

The temperature variation of the threshold is then given by

$$q_1+q_2\frac{\gamma}{V_0}\kappa\frac{h\nu}{k}\Phi'=q_1-q_2\frac{\gamma}{V_0}\kappa\int_0^T C_v dT=q_1-q_2\int_0^T \alpha dT.$$

That means, that for an increase of 100°C and $q_2\sim 5$ volts, the change in the photoelectric threshold is as follows.

K	Al	Mg	Zn	Cu	Ag	Au	Fe	Ni	Pt	Pb	Sb	
125	36	39	43	25	29	21	17	23	15	43	18	millivolts.

Comparing this with experiments, it seems reasonable that such a change could not be detected in the work of Millikan and Winchester[24] who heated Al, Mg, Zn, Cu, Ag, Au, Fe, Ni, Pb, Sb 100° and of Varley and Unwin[25] who varied the temperature of Pt 300°, corresponding to changes of less than 50 millivolts. It is more astonishing that Millikan and Winchester[24] found no change for Al between 50 and 350° (110mv) and Ladenburg[26] for Au, Pt, Ir up to 860° (150mv) and that Dember[27] could not detect any effect on K on heating it to 67°, but it is difficult to estimate how much a change in the long-wave-length limit would affect the current measured by these investigators.

Recently Du Bridge[28] detected a change in current upon heating platinum to 1200° and narrowed down the wave-length shift to a region between 1943-1973A; 30A would correspond to 90 while $q_2\sim 5\,V$ would lead to 180mv. Measurements of Suhrmann[29] give a few percent shift in Ag, Au, Pt between room temperature and liquid air. Finally Ives[30] has found a shift for K in the same interval of 220mv while $q_2=5$ would give 250 (actually it should be less on account of the smaller coefficient of expansion at low temperatures). It seems therefore that the present theory gives the right order of magnitude.

It should be mentioned in conjunction with the fact that the oxide-coated cathodes have a particularly high A', that Koppius[31] found a very strong variation of their threshold with the temperature.

[24] R. A. Millikan and G. Winchester, Phil. Mag. **14,** 188 (1907).

[25] W. M. Varley and F. Unwin, Proc. Roy. Soc. Edinburgh **27,** 117 (1907).

[26] R. Ladenburg, Verh. d. D. Phys. Ges. **9,** 165 (1906).

[27] H. Dember, Ann. d. Physik **23,** 957 (1907).

[28] L. A. DuBridge, Phys. Rev. **29,** 451 (1927).

[29] R. Suhrmann, Zeits. f. Physik **33,** 63 (1925); see also A. Becker, Ann. d. Physik **78,** 83 (1924).

[30] H. E. Ives, Journ. Am. Opt. Soc. **8,** 551 (1924); H. E. Ives and A. L. Johnsrud, Journ. Am. Opt. Soc. **11,** 565 (1925).

[31] O. Koppius, Phys. Rev. **18.** 443 (1921).

III. Justification of Method of Procedure

1. We have made our calculations as if the evaporating electron were taken from the interior and have not said anything in particular about the surface. Here we have to distinguish two steps in the equilibrium condition (7) we have put the expression for the thermodynamical potential of an electron deep in the interior of the vessel equal to one in the gas. But as Schottky pointed out, this is justified as the numerical value of μ (not the form of μ) must be the same for an electron in the interior as it is in the surface on account of the internal equilibrium of the electrons. On the other hand, the particular expression for the potential energy (q) in the interior, as calculated by Bethe, might be wrong; this value might be influenced by the surface. But it seems reasonable that this would not change the order of magnitude of q_z, and our calculation does not claim more.

2. We did not include, "electrical contributions," as we defined the Volta potential ϕ as being due to the total charge and we assume this to be zero (compensation for Volta potential in the actual thermionic experiment). The difference between this case and the usual case, for example in the thermodynamics of gases where differentiation at constant pessure (analogous to ϕ) and constant volume (analogous to en) makes a difference even for $n=0$, comes from the fact that

$$pV = nkT$$

and therefore $\partial(pV)/\partial n = kT$ even for $n=0$ while here $ne\phi$ is proportional to n^2 and therefore $[\partial(ne\phi)/\partial n]_{n=0}=0$.

The reason we have deviated from Schottky's[13] definition, which amounts here to saying that the non-electric part in the differences of the (total and free) energy is the one remaining, if the two places to be compared were brought to the same potential, is the following: With this definition all differences in potential energy of the electron would belong to the electrical part. Indeed, the electrical potential of a place is defined only by the work necessary to bring a test charge (electron) there. Accordingly the difference in potential energy q inside and outside of the metal would belong entirely to the electrical part, which does not seem advisable. On the other hand, it is always possible, by measuring at a sufficient distance, to state whether a (large) body is charged. We define as the non-electric part of the (free or total) energy of an electron in respect to a (large) body the part which would be alone present if the body as a whole were uncharged.

In passing, it may be said that this together with the emphasis that in measuring thermionic currents one has always to correct for the Volta potential, that is one always takes care to have $\phi=0$, gives a clear view of the situation in the presence of surface layers.

3. We have assumed that Φ or the specific heat C_v of the metal at constant volume depends upon n only indirectly through the volume. If we now drop this assumption, (8) and (13) remain unchanged, but in (7) we must add

$$-T\left(\frac{\partial}{\partial n}\Phi\right)_{v,T}=-\frac{h}{k}\Phi'\frac{\partial \nu}{\partial n}$$

which then produces finally on the right hand side of (17) another factor

$$\exp\left[\frac{h}{k^2T}\Phi'\frac{\partial \nu}{\partial n}\right].$$

Now we can write, for a plate containing N atoms, at sufficiently high temperature

$$\frac{h}{k^2T}\Phi'\frac{\partial \nu}{\partial n}=-\frac{h}{k^2T}3Nk\frac{kT}{h\nu}\frac{\partial \nu}{\partial n}=-3N\frac{\partial \ln \nu}{\partial n}$$

or better

$$-\partial(\Sigma \ln \nu)/\partial n$$

where the sum is to be extended over all the vibrations which make up the heat movement of the plate. Therefore[32]

$$\exp\left[\frac{1}{R}\left(\frac{\partial \Phi}{\partial n}\right)_{v,T}\right]=\prod_i \exp\left[-\left(\frac{\partial \ln \nu_i}{\partial n}\right)_v\right].$$

If we would assume that the removal of an electron affected only three vibrations (in a primitive picture the vibrations of one atom), we could say safely that the new frequency would lie between half and the double of the original frequency, or

$$\left|\frac{\partial \ln \nu_i}{\partial n}\right|<1 \quad i=1,2,3 \quad \frac{\partial \ln \nu_i}{\partial n}=0 \quad i>3.$$

Then, the additional factor in (19) woud lie between e^{-3} and $e,^3$ 1/20 and 20. If, as will be the case, the change affects all vibrations, it still seems reasonable that

$$\left|\sum\frac{\partial \ln \nu}{\partial n}\right|$$

will be not much larger than 3 and therefore, a direct influence of a removal of electrons on the specific heats at low temperature will probably not influence A' as strongly as the indirect effect through the volume.

4. The most important assumption however that we have made is the omission of a part of q which would be explicitly dependent on temperature. Now the part in the potential energy of an electron which is due to the surrounding charges, as calculated by Bethe,[16] is not dependent directly on temperature (the heat movements of the positive ions will upon averaging have no effect of the first order). But there might be another contribution[32] due to

[32] W. Schottky, reference 13, p. 96f. See also E. D. Eastman, Jour. Am. Chem. Soc. **48,** 552 (1926), C. Zwikker, Physica, **9,** 321 (1929).

an electric double layer or space charge, which might be formed on the surface of the metal where the electron density drops gradually off. This might depend on T, not in the part farther in, where the electron density is still high, the electron gas degenerate and therefore its μ independent of T, but in the outside layers. How much these contribute, can not be estimated until a calculation has been made.

The only thing to be said is that the part discussed previously gives the right order of magnitude.

IV. Other Applications

The method which we have devloped here can be applied similarly to an ordinary solution, in which the mutual potential energy between the solvent and the dissolved molecules depends on the distance between them and accordingly varies indirectly with the temperature on account of the heat expansion of the solvent.

CHANGE OF SPACING OF POSITIVE COLUMN STRIATIONS WITH TEMPERATURE

By F. M. Sparks and Charles T. Knipp
University of Illinois

(Received December 19, 1929)

Abstract

Cassen's prediction (Phil Mag. **268,** 948, Nov. 1926) that the separation of the striations in a discharge tube should increase almost linearly with the absolute temperature is verified for the wide blue striations. For the narrow striations, the separation first decreases, but in general reaches a minimum, after which the separation increases as predicted.

FROM theoretical considerations, Cassen[1] predicts that the distance between striations in the positive column of a discharge tube should increase almost linearly with the absolute temperature, and that the addition of an impurity may greatly change the spacing.

A vertical discharge tube was heated in a liquid bath contained in a large vertical glass tube. An electric heating coil was placed in the bottom of the bath and the temperature controlled by an external resistance. Two thermometers were placed in the bath at different heights to obtain the temperature. A large flask was connected to the discharge tube to minimize the change in pressure due to change in temperature of the tube. To secure steady striations which could be measured with a cathetometer, a potential of 3000 volts from small storage cells was used. The current was controlled by a water resistance and measured with a milliammeter.

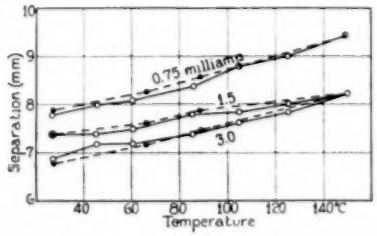

Fig. 1. Wide striations at a pressure of 1 mm Hg.

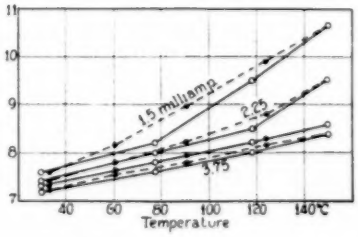

Fig. 2. Wide striations at a pressure of 1 mm Hg.

Hydrogen was used in the discharge tube because it gives striations over a much greater range of conditions than the other ordinary gases. Only the blue striations were obtained, these being due to impure hydrogen.[2] The pressures used were such that both the wide and the narrow blue striations appeared.[3] To detect any temperature lag or change in character of the gas, the separations were noted with both increasing and decreasing temperature.

The separation was gotten by measuring across several striations and

[1] B. M. Cassen, Phil Mag. **268,** 948 (1926).
[2] Handbuch der Physik, vol. 14, p. 298.
[3] Handbuch der Physik, vol. 14, p. 300.

dividing this distance by the number of striations measured. The separation in millimeters was plotted against the temperature of the bath in degrees Centigrade. Measurements were made for different values of the current because the separation varies with current.[4]

Figure 1 shows three curves, obtained at the same time, for current values of 0.75, 1.5, and 3 milliamp. Measurements were begun at room temperature, the unbroken line indicating readings with increasing temperature, and the broken line being for decreasing temperature. Figure 2 shows another set of curves, for currents of 1.5, 2.25, 3, and 3.75 milliamp. Both these sets of curves are for the wide striations, at pressures of about 1 mm Hg. Figures 3 and 4 represent data for the narrow striations, at pressures of 2.5 and 1.7 mm.

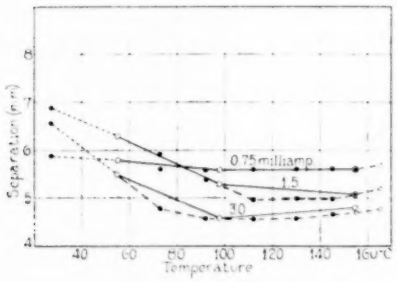

Fig. 3. Narrow striations at a pressure of 2.5 mm Hg.

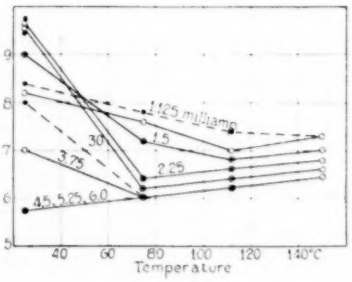

Fig. 4. Narrow striations at a pressure of 1.7 mm Hg.

In Fig. 3 the readings were begun at 155°C, the temperature lowered to 55°, then increased to 165°, and the last readings at room temperature were made the next day. In Fig. 4 no reading was made for a current of 6 milliamp. at 150° because the cathode became too hot. Figures 1 and 3 were made with prepared hydrogen, using one discharge tube, and Figs. 2 and 4 with commercial hydrogen, using a different tube.

Figures 1 and 2, representing the wide striations, agree with Cassen's prediction that the separation should increase almost linearly with the temperature. Figures 3 and 4, representing the narrow striations, show that the separations may first decrease but that they reach a minimum value and then increase linearly with the temperature. The curves for current values of 4.5, 5.25 and 6 milliamp. in Fig. 4 show only an increase in separation, which is in exact accord with the prediction. However, the minimum value of the separation seems to be shifted toward lower temperatures as the current is increased so that these curves might be expected to be similar to the others in the same figure, but with a minimum at some temperature below room temperature. Figure 3 also shows the shifting of the minimum to the left with increasing current. The deviation from Cassen's predictions might be explained by saying that his simplifying assumptions are valid only under certain conditions.

A series of curves was also plotted for hydrogen at 2.5 mm, after successive additions of impurity. The general shape of the curves was similar to those of Fig. 3, but they were shifted down to smaller values of separation, reaching a minimum, and then were shifted up to greater values.

[4] Handbuch der Physik, vol. 14, p. 301.

PERSISTENCE OF VELOCITY AND THE THEORY OF SECOND ORDER GAS REACTIONS

By Louis S. Kassel*
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(Received December 10, 1929)

Abstract

R. H. Fowler has stated that if, in second order gas reactions, it is supposed that reaction occurs whenever two reactant molecules collide with sufficient velocity, then the deviation from the Maxwell distribution law which would result is so great that this law cannot be used in calculating the rate of the reaction. It is shown that this view is sometimes in error, and that in a mixture of molecules of nearly equal mass reacting in this way the molecular velocities do not diverge appreciably from the predictions of the Maxwell law.

IT IS an experimental fact that the rates of all the known second order gas reactions can be represented, at least within a factor of 5 or 10, by the simple expression $Ze^{-E/RT}$, where Z is the number of collisions between reactant molecules, calculated in accordance with the methods of kinetic theory, and E, the energy of activation, is an experimental constant for each reaction. There are a number of simple theories which are able to predict an equation of this form. In particular, if it is assumed that reaction occurs at every collision for which the relative velocity parallel to the line of centers at the instant of collision is at least V_0, it is found[1] that the rate is $Ze^{-E_0/RT}$, where $E_0 = MV_0^2/2$ and M is the reduced molecular weight $M_1M_2/(M_1+M_2)$. If it is supposed that the reaction occurs whenever the relative velocity of the collision exceeds V_0, regardless of its direction with respect to the line of centers, it is found that the rate is given by $Ze^{-E_0/RT}(1+E_0/RT)$. Since in actual cases E_0/RT is about 40, the form of this equation is not experimentally distinguishable from a simple exponential, though of course the predicted rate, for an experimentally determined temperature coefficient, is rather larger. This latter mechanism has been considered recently by Fowler[2] from the standpoint of persistence of velocity;[3] he has concluded that if reaction were to occur at every collision the number of high velocity molecules present in the gas would fall far below the Maxwell quota, so that the rate of reaction would be substantially less than that calculated; if the mechanism of any actual second order reaction were of this simple type, and if the theory were subject to the correction suggested by Fowler, then we should expect the rate to be very considerably increased by the addition of an inert gas, which would tend to maintain the Maxwell quota, and an effect of this kind has not been observed.

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[1] See, for example, Tolman, Statistical Mechanics, (1927) p. 272.

[2] R. H. Fowler, Statistical Mechanics, (1929), p. 461.

[3] Jeans, Dynamical Theory of Gases, (1925), pp. 260, 275, 312.

It seems, however, that when the molecular masses are nearly equal Fowler's correction is actually inappreciable; qualitatively this is so because in most of the collisions with relative velocity of V_0 or more, each of the colliding molecules has velocity of about $\frac{1}{2}V_0$; hence if reaction did not occur, each of them would leave the collision with velocity about $\frac{1}{2}V_0$, and, since this is very much greater than the mean velocity of all the molecules, in the vast majority of cases each of them would next collide with a slower molecule; at such a collision the relative velocity could not be greater than V_0, so that reaction could not occur. Fowler has written, "A certain proportion of collisions with relative energy more than ξ will concern at least one molecule whose last collision was also one of the same class. This is the phenomenon *of the persistence of velocities*." This, however, is not exactly what Jeans has meant by the term; he has taken as a measure of the persistence the ratio of the expected component of velocity after the collision in the direction of the original velocity to this original velocity, and found for this ratio a value of about 40 percent. Fowler is interested not in this, but in the value of the proportion mentioned in the preceding quotation, which is a very different thing.

Since an exact calculation would involve the quadrature of some rather cumbersome integrals, it will be considered sufficient to show that the effect in question is very small. First we notice that almost all of the collisions with relative velocity greater than V_0 have relative velocity less than $9V_0/8$; the ratio of the number which exceed this limit to the number which exceed V_0 is about $e^{-17E_0/64RT}$, which is of the order of 10^{-4}.[4] We shall use the methods given by Jeans.[5] Instead of the three velocity components for each of the two molecules which are involved in the collision, we take three for the center of gravity, and three for the relative velocity. When we do this, we find that, both before the collision and afterwards, the relative velocity of each molecule is about $\frac{1}{2}V$. Jeans' treatment shows that the motions of the centers of gravity of the various collision complexes obey the Maxwell law for molecules of the appropriate mass, and that there is no correlation between the relative velocity of the collision and the velocity of the center of gravity of the colliding molecules. Since this is so, we can calculate the chance that the relative velocity of the center of gravity and the next molecule with which either of the original ones will collide shall exceed any specified value. We have seen that only in a negligible fraction of the collisions which concern us will the relative motion of the center of gravity of the colliding molecules and either of the molecules exceed $9V_0/16$. Now it is plainly necessary (though not sufficient), in order for the relative velocity of the next collision to exceed V_0, for the relative velocity of the colliding molecule and the center of gravity of the two original molecules to exceed $7V_0/16$. This chance is easily calculated as about 10^{-3}. Hence we may state confidently that the proportion in which Fowler is interested is less than one in a thousand, and may be neglected. A similar treatment can be given for the case that the relative velocity along the line of

[4] In all the following calculations, the value 40 will be used for E_0/RT.

[5] Jeans, reference 3, p. 35.

centers must exceed a critical value for reaction to occur. Hence the simple expressions $Ze^{-E_0/RT}$ and $Ze^{-E_0/RT}(1+E_0/RT)$ are the correct rate expressions for the mechanisms which have been described when the molecular masses are nearly equal.

When the masses of the two molecules are very different, the situation is entirely changed, and the correction discussed by Fowler becomes of importance. Thus in a collision between a molecule of hydrogen and a molecule of iodine, where the ratio of the masses is about 127, the hydrogen contributes practically all the velocity of the collision; in a large fraction of all the collisions with relative velocity greater than V_0, the hydrogen molecule itself has a velocity greater than this value, and can be expected to produce another collision of the same type if it survives the first one. The correction would be most important when the concentration of hydrogen was much less than that of iodine; then hydrogen molecules would have been expected to execute fairly long series of collisions with iodine, all with relative velocity greater than V_0, if the system did not react; the reaction mechanism which has been postulated would cut off these series at the first member, and the rate would therefore be much less than that given by the naive calculation. There is no experimental evidence for such behavior, which indicates either that this is not the mechanism of the reaction or that if it is, then reaction occurs only at a small fraction of the collisions for which the energy condition is satisfied.

With regard to the question of the actual mechanism of second order reactions, the writer does not believe that either of these simple mechanisms is correct. It seems likely to him as it does to Fowler also, that translational, vibration, and rotational energy must all be considered, and that in most cases the effective target area for reaction will be small compared to the kinetic theory cross-section.

YOUNG'S MODULUS DETERMINED WITH SMALL STRESSES

By Darol K. Froman
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(Received December 19, 1929)

Abstract

An interferometer method similar to that used by E. Grüneisen was used to determine the extensions of metallic rods of brass, steel, copper, aluminum and nickel under small stresses. The largest stresses applied were considerably less than those usually used in commercial testing. For the substances examined Young's Modulus was found to increase very rapidly as the stress increased from zero, reach a maximum at a comparatively small stress, and then to decrease almost exponentially to the ordinary value. The annealing of the rod may be connected with this divergence from Hooke's law with small stresses, as slight differences were found on reannealing some of the rods used.

IT HAS been known[1] for some time that the value of Young's Modulus computed from the velocity of weak longitudinal vibrations in rods was appreciably higher than that obtained by ordinary static methods. The differences expected in the adiabatic and isothermal moduli[2] are small compared to those found experimentally by dynamic and static methods, although values found by these methods are often quoted as the adiabatic and isothermal moduli respectively.[3] Therefore it was decided to measure the elasticity statically at small stresses, comparable with those in a sound wave. Following E. Grüneisen[4] an interferometer was used to determine the strain.

In Fig. 1 the rods A are under test and the plates B are fixed to their ends. There is a universal joint at the point C. G and H are plates with holes and lock screws to clamp them to the rods. The holes are bevelled so that contact with the rods A can be made at one point only. By means of rods P the plate G supports another plate E, having a circular hole in its centre under which is supported a three-quarter silvered mirror T. The plate H has three levelling screws supporting a plate Q, on which is placed the other interferometer mirror R, similar to T. N is a right-angled prism held in position by a fixed external support and L is a mirror also supported from the outside. S is the source of light, a mercury arc, used with a filter F.

Monochromatic light is incident on L and reflected through the partly silvered mirrors to N, which totally reflects it to the telescope M. The telescope is adjusted for parallel light and circular interference fringes can be produced by making the mirrors R and T parallel with each other. The telescope is equipped with an eye-piece having both movable and fixed cross

[1] R. J. Lang, Proc. Roy. Soc. Can. **16,** 163 (1907). G. W. Pierce, Am. Acad. Proc. **63,** 1 (1928). E. Grüneisen, Ann. der Physik **22,** 801 (1907).

[2] G. F. C. Searle, "Experimental Elasticity" p. 22.

[3] E. Grüneisen, reference 1, p. 843.

[4] E. Grüneisen, reference 1, p. 826.

hairs. W is a scale pan attached to the center of the lowest plate by means of a universal joint not shown in the diagram. As weights are applied at W the rods A stretch, the mirrors separating by the extension in the length from G to H. This causes the fringes to move out from their center. Three vanes not shown in the diagram are clamped to the bottom plate. These move in an oil bath to damp the motion of the apparatus after the application of a weight at W.

Measurements were made by taking the diameters of two successive fringes in the arbitrary units of the screw attached to the movable cross hair. Then a weight was applied to W and the number of fringes passing the cross

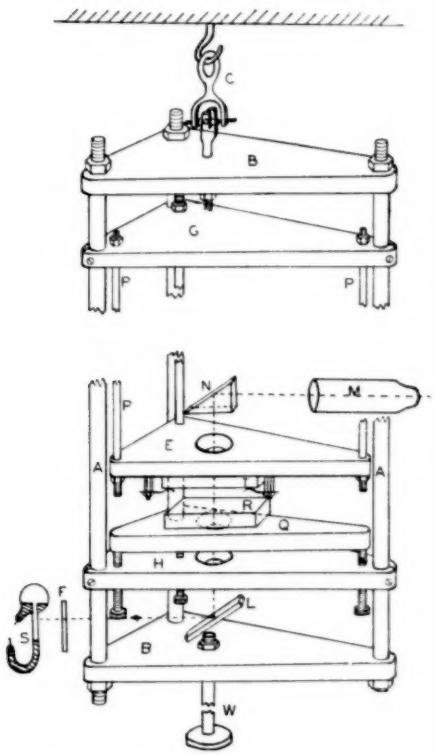

Fig. 1. Diagram of interferometer.

hairs counted. The diameter of the fringe which remained between the positions previously occupied by the two fringes measured was then taken. If readings were taken on fringes further from the center than the fourth or fifth, no appreciable error was introduced by taking the fractional fringe shift as proportional to the displacement over the width of one fringe. Thus if d_1 and d_2 be the diameters of two successive fringes, and, on the application of a weight, n fringes and a fraction pass the cross hairs, if d_3 be the diameter of a fringe occupying a position between d_1 and d_2, then the fringe shift is $n+(d_3-d_1)/(d_2-d_1)$.

Since a shift of one fringe is caused by a motion of the mirrors R and T of one-half wave-length, the extension in the part of the rods from G to H can be computed, and Young's Modulus found in the usual way by dividing the stress by the strain.

Care was taken to keep the apparatus at a nearly constant temperature as the difference in the lengths of the rods P and A produces a different thermal expansion. The two sets of rods must be of the same material, also, so that their thermal expansion coefficients will be equal. It was found that if one set were of brass and the other of steel, temperature changes of one degree

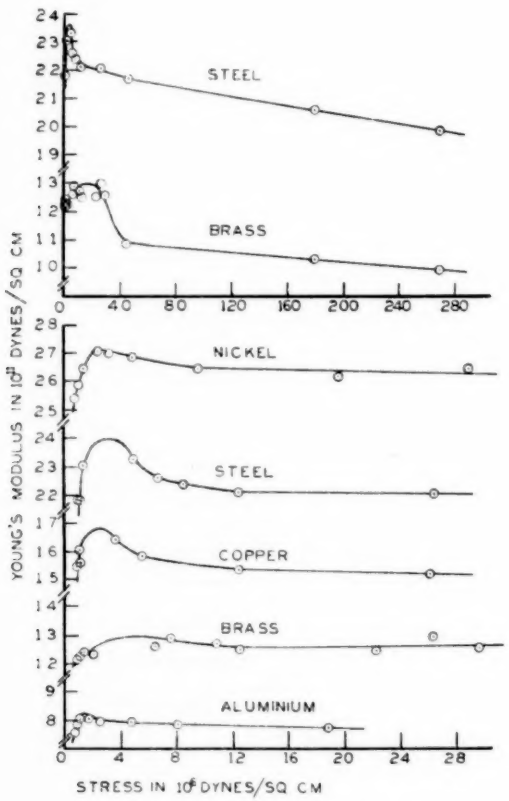

Fig. 2. Curves of Young's Modulus.

per hour were quite sufficient to invalidate the results since it required two or three minutes to take a reading.

After a reading was taken the weight was removed and the diameters of the fringes checked to see if the rods had returned to their original lengths. if they had not, the reading was thrown out. It was found quite easy to measure the displacement of the mirrors to one two-hundredth of a wave-length.

The stress on the rods was adjusted to any desired value by applying weights at W and the elasticity measured by applying a small additional

weight and measuring the shift in the fringes. The stress was computed from the sum of the original weights at W, one-half of the small additional weight and the weight of the parts of the apparatus supported by the rods including one-half of their own weight.

In this way Young's Modulus was determined for five materials at various stresses. The rods used were about 40 cm long and 0.95 cm in diameter. In Fig. 2 curves of Young's Modulus against stress are plotted for the various materials.

Professor Huntley of Armour Institute, Chicago, kindly determined Young's Modulus for two of the specimens at three very much higher stresses than it was possible to use with the apparatus just described. The rods used were cut from the same piece as the ones tested with the interferometer. These values are the three with largest stresses plotted in Fig. 2 for steel and brass, respectively. By means of Kundt's tube the velocity of sound was measured in each material. The air in the tube was carefully dried and Young's Modulus, E, calculated from the relation

$$v = \sqrt{E/d},$$

where v is the velocity of sound and d is the density. The values obtained by this method are given in Table I.

TABLE I. *Young's Modulus as determined from velocity of sound.*

Material	v(cm/sec)	d(gm/cm^3)	E(dynes/cm^2)
Brass	3.63×10^5	8.45	11.1×10^{11}
Steel	5.15×10^5	7.81	20.75
Copper	3.89×10^5	8.61	13.01
Aluminum	5.155×10^5	2.70	7.19
Nickel	4.905×10^5	8.82	21.25

For two of the materials rods were excited into longitudinal vibrations at various frequencies up to 17000 per second, by a method described by Boyle and Lehmann.[5] The rods were cut in half and each glued, end on, to a thin piece of quartz cut with its faces perpendicular to an electric axis. This constituted a parallel-plate condenser which was connected in parallel with the variable condenser in the tank circuit of an ordinary five watt radio oscillator. Then the faces of the quartz disc were vibrated longitudinally by the piezo-electric pressures and the frequency of the electric oscillations varied until the rods came into resonance. If this frequency were in the audible range of frequencies the rods gave off a distinct sound. A precision wave-meter was used to determine the frequency of the Hertzian oscillations which was, of course, the frequency of the mechanical vibrations of the rod. In agreement with Professor Pierce,[6] this was found to be constant at all of the frequencies tried and the same as that given by Kundt's tube, although the stresses were probably much smaller.

[5] Boyle and Lehmann, Trans. Roy. Soc. Can., Sect. III, Vol. XIX (1925).

[6] Pierce, Am. Acad. Proc. **63,** 40 (1928).

A set of steel rods were annealed in an electric furnace and the tests again carried out. Young's Modulus was found to be slightly higher for each value of the stress that it was previously. Otherwise the behavior was exactly similar.

From these results it appears that Hooke's Law does not hold exactly for very small stresses but that Young's Modulus has a maximum at some small but finite stress. The elasticity decreases rapidly to the ordinary value as the stress is increased from this value and decreases even more rapidly as the stress is decreased from the point of maximum elasticity. It will be noted that Young's Modulus determined from the velocity of sound is somewhat lower than the values from the interferometer method but higher in the cases of brass and steel, than the values obtained with large stresses.

In conclusion the author wishes to acknowledge with thanks the assistance given by Professor Huntley of Armour Institute, mentioned above, and to thank Professor Dempster of this Laboratory for his untiring interest in the problem and his many very valuable suggestions.

ROCHELLE SALT AS A DIELECTRIC

By C. B. Sawyer and C. H. Tower
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(Received November 6, 1929)

Abstract

Both saturation and hysteresis appear in Braun tube oscillograms made at various temperatures with a condenser whose dielectric consists of Rochelle salt slabs cut perpendicular to the a-axis. The dielectric constant for such slabs may reach a value of 18,000. Curves are also given, showing the variation in mechanical and electrical saturation with temperature. These correspond in only a general way to the piezoelectric constant's variation with temperature. Certain marked peculiarities are noted in the resulting mechanical deformation when Rochelle salt is excited with alternating potentials. Clear Rochelle salt half-crystals have been produced up to forty-five centimeters in length.

THE remarkable physical properties of Rochelle salt, the most piezoelectric active of all crystalline substances, have been reported by other authors.[1] Comparatively small plates and few crystals were used in their determinations.

Work at this laboratory has been carried on for a number of years on Rochelle salt with a view towards commercialization. It has, therefore, been necessary to produce large clear crystals in quantity. Clear, flawless half-crystals are grown up to 45 cm in length and 2 kg in weight.

The dielectric strength and insulation value of plates from such crystals is very high. Many hundreds of plates (mostly perpendicular to the a-axis of the crystal) have been produced and their electrical properties measured. Thus a Rochelle salt plate 4.75 mm thick shows a dielectric constant of 18,000 when tested at 15°C at 60 volts 60 cycles alternating current. The highest previously reported value which has come to the attention of the authors is about 1380.[2] An air condenser of area and capacity equal to that of the crystal plate would have a plate separation of only 0.00475 mm, if 1380 be taken as the crystal dielectric constant; and 0.000262 mm (0.0001″) if 18,000 be taken. It is thus evident that a comparatively thin layer of cement or dehydrated Rochelle salt between the body of the crystal and the foil electrode will introduce a very large error in the determination of the dielectric constant. Any adhesive such as balsam in xylol, Japan Gold size, or beeswax dissolved in benzol with a small addition of rosin, may be used in dilute solution for atttaching the foil. It is important, subsequently, to

[1] Frayne, Phys. Rev. **21,** 348 (1923); Isley, Phys. Rev. **24,** 569 (1924); Laurey and Morgan, J. Am. Chem. Soc. **46,** 2192–6, (1924); Pockels, Encyklopadie der Math. Wiss. Vol. 5, Part 2; Valasek, Phys. Rev. **17,** 475 (1921); **19,** 478 (1922); **20,** 639 (1922) and **24,** 560 (1924). Voigt, Lehrbuch der Kristallphysik, Chap. 8, Leipsig (1910).

[2] Valasek, Phys. Rev. **19,** 488 (1922).

rub down the foil very thoroughly to bring it as close to the crystal surface as possible.

A series of Braun tube oscillograms was obtained. For this purpose, and for all other results reported in this paper, a crystal plate was employed measuring about $8.5 \times 5.5 \times 0.5$ cm, cut with its plane perpendicular to the

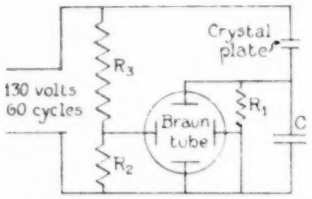

Fig. 1. Schematic connection of Braun tube. Capacity of crystal plate 0.004 to 0.2 Mf; of C 0.7 Mf. $R_1 = 0.45$ megohms; $R_2 = 3180$ ohms; $R_3 = 31800$ ohms.

a-axis, and its long edges parallel to the c-axis. All measurements and oscillograms were carried out with 60 cycle current from the power lines. All vertical deflections are on the same scale as in Fig. 2.

Fig. 1 shows the connections employed with the Braun tube for obtaining crystal oscillograms. At the left is a resistance acting as a voltage divider. To the right is the crystal plate under test, connected in series with a con-

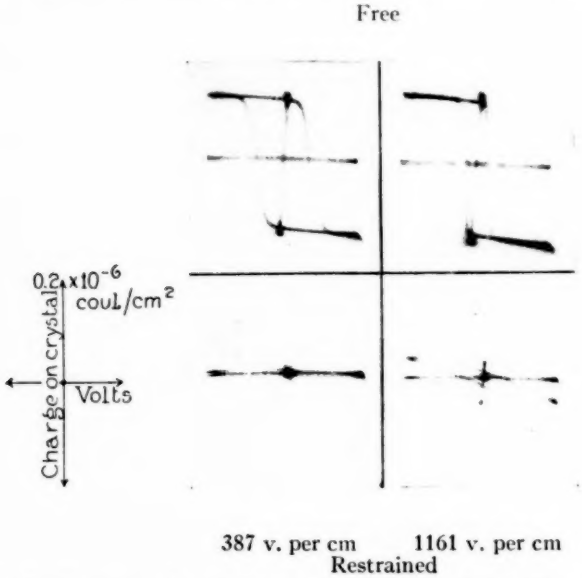

Fig. 2. Oscillograms of crystal plate, free and restrained. Temperature 15° C; frequency 60 cycles per sec.

denser giving voltages proportional to the charge on the crystal. The resulting oscillograms, such as shown in Fig. 2, have ordinates proportional to crystal charge and abscissae proportional to applied voltage.

Fig. 2 shows comparative oscillograms of a plate when entirely free, and of the same plate restrained by cementing it between two thick aluminum

plates, thus very largely precluding mechanical motion due to piezo-activity. The left-hand vertical pair is for 387 peak volts per cm; the right-hand vertical pair is for 1161 peak volts per cm. The upper pair is unrestrained; the lower pair is restrained. Dielectric constants calculated from these oscillograms show exceedingly interesting and suggestive values: from the left-hand oscillogram (restrained plate) about 430; from the left-hand oscillogram (free plate) in the saturated range about 330; from the same oscillogram for a complete cycle, excluding saturation range 10,500; and for maximum instantaneous value not less than 200,000.

Such enormous values of the dielectric constant in connection with less efficient foiling of the crystal plates, may account in part for the previously observed storage battery effect. Supplementary tests indicate that little

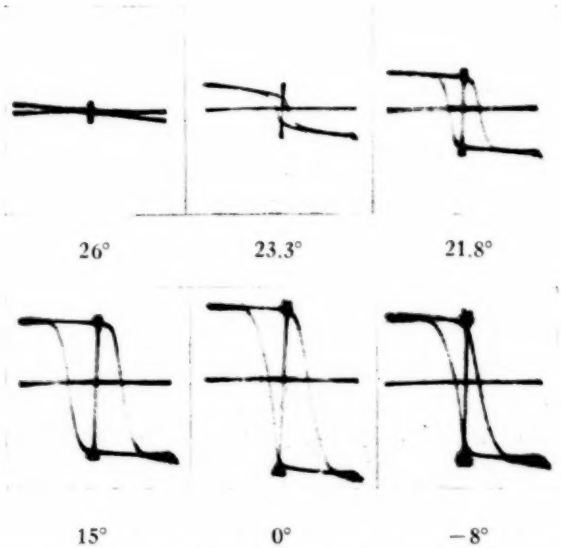

Fig. 3. Hysteresis and saturation of Rochelle salt plate II. Potential gradient in dielectric 387 (peak) volts per cm; frequency 60 cycles per sec.

change in the value of the dielectric constant is to be looked for as a result of improvement in foiling. In these supplementary tests, electrodes of saturated Rochelle salt solution were used and results did not differ significantly from those obtained from a carefully foiled plate. Moreover these large values of the dielectric constant of Rochelle salt have been observed in many hundreds of plates of various dimensions from many different crystals. Determination of the dielectric constant was usually made by applying 112 volts of 60 cycles alternating potential to the free crystal plate and noting the resulting current. In addition, circuit resonance and condenser substitution methods served to check this first method, all three giving results in substantial agreement.

Fig. 3 comprises a series of comparative oscillograms made from the same crystal plate at different temperatures as indicated. Proceeding from top

left to bottom right it is evident that as the temperature is decreased both the voltages and charges required for saturation greatly increase. So also do the areas of the hysteresis loop. Here again the method of applying the foil electrodes to the crystal is of great importance as the shape and area of the loop will vary somewhat with this factor.

All of the oscillograms were made with the greatest care. A second crystal plate gave results identical with the first. Two other plates of the same dimensions as before but with their long edges cut at 45° to the c-axis, showed no essential differences in the derived oscillograms. Though no special humidity precautions were observed, the resistance of the plates, at 100 volts constant potential, never fell below many megohms.

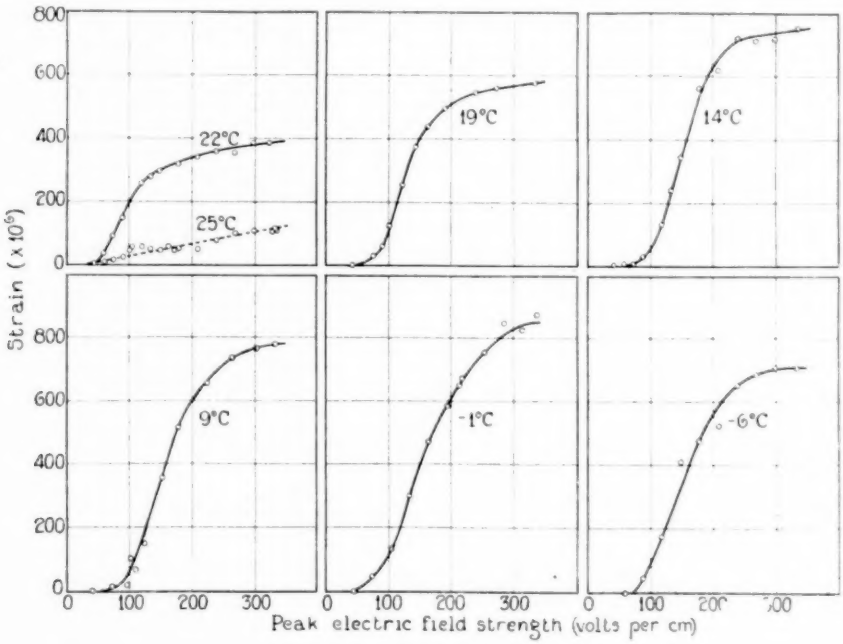

Fig. 4. Temperature variation of saturation effect and piezoelectric constant.

If a standard plate—its long edge being cut parallel to c-axis—is electrified with an alternating potential, it will be deformed and such deformation can be observed and measured conveniently with a microscope. For the results shown in Fig. 4, one short edge of the plate was cemented to a large lead block and various values of 60 cycle potential were applied to the electrodes. The alternating motion produced under these conditions lies in the plane of the plate and is perpendicular to the c-axis. The relation between total deformation and electrification is shown for various temperatures.

Saturation is again in evidence and saturation values again increase greatly with decrease in temperature. Keeping close pace with it is the voltage required to produce saturation. But it is very noteworthy that considerable voltage must be applied before the crystal shows appreciable deformation.

Fig. 5 shows the close relationship existing at different temperatures between: 1st, volts per cm required for mechanical saturation; 2nd, the energy loss per cubic centimeter per cycle; 3rd, the charge per cubic centimeter required for electrical saturation. Though not shown in this figure, these curves are followed closely by those of the voltage required for electrical saturation and of the deformation at mechanical saturation. No determina-

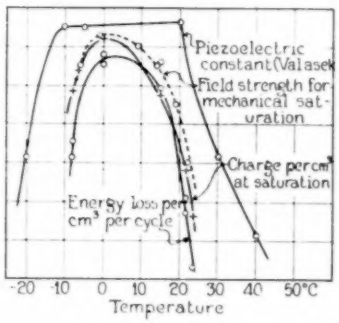
Piezoelectric constant (Valasek)
Field strength for mechanical saturation
Charge per cm³ at saturation
Energy loss per cm³ per cycle
-20 -10 0 10 20 30 40 50°C
Temperature

Fig. 5. Properties of Rochelle salt at various temperatures.

tions of the piezoelectric constant were made, but Valasek's[3] most recent curve of the temperature variation of the piezo-electric constant is included for the sake of comparing temperature variation of this property with those of the others.

It has been the great privilege of the authors to carry on this work begun under the very able leadership of the late Charles F. Brush, Jr.

[3] Valasek, Science Vol. LXV No. 1679, p. 235 (1927).

SEDIMENTATION EQUILIBRIA OF COLLOIDAL PARTICLES*

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(Received December 9, 1929)

Abstract

The purpose of this work was to find the distribution law of colloidal particles for sedimentation equilibrium in large cells, in which uniform concentrations had been observed by Burton, Porter and Laird. We took great care to eliminate effects which might prevent an equilibrium state. Gold particles prepared by the Zsigmondy nuclear method were allowed to settle several days in a quartz cell in a carefully controlled thermostat bath. The steady state was determined by taking visual ultra-microscopic counts on different days. The La Place-Perrin exponential law of distribution was found to hold as demanded by the kinetic theory.

Introduction

UNTIL recent years it seemed quite well established that colloidal particles obey in their Brownian movement and related phenomena the simple laws of the kinetic theory when no forces operate between the particles. Thus, in the early work on sedimentation equilibria with colloids in a gravitational field, Perrin[1] and Westgren[2] found results in agreement with the familiar La Place-Einstein distribution law, which the molecules of the atmosphere obey; namely:

$$\log n = \log n_0 - Nvgh(\rho_1 - \rho_2)/RT.$$

In this equation n is the concentration of particles at the height h above a given point of reference, n_0 is the concentration of particles at the reference point, v is the volume of a particle, ρ_1 is the density of the particles, ρ_2 is the density of the medium in which the particles are dispersed, g is the gravitational acceleration constant, R is the gas constant and T is the absolute temperature. Each of the two above-mentioned men used cells constructed of microscope slides and cover glasses, the depth of the cells used by Perrin being in general about 0.1 mm. The very careful work of Westgren, who observed through ranges as great as 1.1 mm in thin cells of presumably much greater depth than the range of observation, yielded a value of N which checks very closely the accepted value.

* This paper contains results obtained in an investigation on the La Place-Perrin Law of the Distribution of Suspensions listed as Project No. 34 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

** American Petroleum Institute Research Fellows.

[1] Perrin, "Brownian Movement and Molecular Reality," page 41.

[2] Westgren, Zeits. f. Phys. Chemie **89**, 63 (1915).

However, later workers in the field of colloids noticed that the particles in larger containers often remained in suspension over long periods of time without any apparent sedimentation. This seemed to be in contradiction with the La Place-Einstein law and investigations on distributions in sols five millimeters or more in depth were carried out by Burton,[3] Porter[4] and Laird,[5] who reported a uniform distribution throughout the greater portion of the sol. In attempts to explain such a distribution, Burton suggested the existence of electrical forces acting between the particles while Porter assumed that his sol was so concentrated that the osmotic pressure of the colloidal solution no longer followed the simple law of dilute solutions; in other words, he introduced a volume term which acts like the b in van der Waal's equation. Although Porter introduced the b term arbitrarily, he suggested that if it should have a physical significance, in order to get the requisite size he must assume a concentration of the liquid upon the particles of the suspension. Others have suggested that the apparent contradiction might be due to insufficient precautions in the eliminating of convection or insufficient time in waiting for the attainment of the equilibrium of colloids in deep cells. Kraemer[6] has made a very illuminating discussion of the whole field, so that it is hardly necessary to present a great amount of critical detail.

At this point, it might be well to mention that Rinde[7] has determined the equilibrium distribution of gold colloids in a high centrifugal field produced by an ultra-centrifuge. The range shown in his plot extends over a distance of more than three millimeters and although the exponential law seems to hold in a layer about 0.5 mm thick, there is a slight deviation from this law in the remainder of the distance.

Since some knowledge of the electrical nature of colloids had already been gained from the study of electrocapillary phenomena, the possibility of forces acting between colloidal particles in such a manner as to become manifest in sedimentation equilibria was of great interest. In fact, the possibility of any factor which would upset the La Place-Einstein law seemed very important for the understanding of all phenomena in which finely divided matter is in contact with liquid. Thus, it seemed worth while for us to attack the problem of sedimentation equilibria in deep cells taking great care to eliminate spurious effects, which might account for a uniform distribution, in particular to avoid convection currents in the sol, to prepare colloids with little variation in size, and to wait a sufficient time for equilibrium to be attained.

Experimental Work

In our work, we used gold sols enclosed in a cell 8.3 mm in height. This cell was constructed of quartz which is much more insoluble in water than glass.

[3] Burton and Bishop, Proc. Roy. Soc. **A100,** 414 (1922); Burton and Currie, Phil. Mag. **47,** 721 (1924).

[4] Porter and Hedges, Phil. Mag. **44,** 641 (1922).

[5] Laird, Jour. Phys. Chem. **31,** 1034 (1927).

[6] Kraemer, "Colloid Symposium Monograph," Vol. V, p. 81.

[7] Rinde, Diss. Upsala, p. 200 (1928).

It is important not to pollute the sol since gold sols are quite sensitive to electrolytes as regards stability. The colloidal solution was allowed to settle undisturbed for several days inside a thermostat system which was capable of holding the temperature constant to within a few thousandths of a degree Centigrade. It was necessary that temperature gradients, which cause disturbing convection currents in the cell, be avoided. The distribution curve was then found by taking visual ultra-microscopic counts at successive levels within the cell's height. The thermostat control was so little affected by the heat from the arc and the observer during the period of observation that there was a temperature rise of only a few thousandths of a degree Centigrade. Thus, the distribution could be determined and compared on different days.

A cross section of the cylindrical quartz cell is shown in Figure 1.

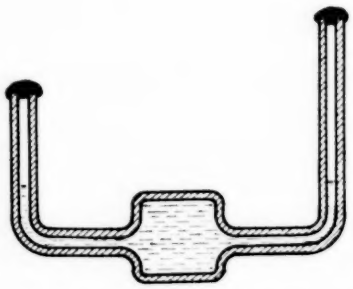

Fig. 1. Cross section of cylindrical quartz cell.

The vertical wall was made of tubing about 8 or 9 mm in inside diameter, the ends of which were ground in order that flat plates could be fused on to form the top and bottom of the cell. The two small L-shaped tubes were sealed into opposite sides of the tubing in order to make possible cleaning and filling of the cell. After the filling with colloidal solution, these side tubes were closed with sealing wax as shown in the diagram.

A great amount of effort was spent on the phase of the problem having to do with temperature control. In the final system, the cell was clamped inside a trough well insulated thermally inside the wooden case marked *C* in the photograph in Figure 2. The cell was immersed in a stream of water, pumped through the trough from a large thermostat tank whose dimensions were $16'' \times 18'' \times 27''$. The connections between the trough and the tank were made inside the insulating material shown in the lower left hand corner of the photograph. The temperature of the water in the trough was obtained by means of the Beckmann thermometer *B*. A view of the assembled apparatus is shown from the opposite side in the photograph in Figure 3, in which the tank is marked *T*. The water was kept in turbulent motion in the tank by means of a large stirring propellor which was rotated by the motor as seen in the photograph. Immersed in this tank was a thermostat regulator made of glass tubing filled with carbon tetrachloride, which has a high thermal coefficient of expansion. This regulator operated a relay to the heating element by means of a vacuum tube circuit mounted on the top of the tank near-by the

relay. With this circuit practically no current flowed through the mercury contact in the regulator.

In Figure 3 a part of the optical system can be seen mounted on the sturdy wooden frame to the left of the tank. The entire optical system was built on the heavy metal carriage *L*. The colloidal solution was illuminated by means of the carbon arc *A*, the light from which was passed through the copper chloride absorption cell *H* in order that the beam which was transmitted should have little heating effect. Next the beam was passed through a paraboloidal condensing lens, a16 mm microscope objective and a glass window in the trough immediately in front of the cell. The beam was transmitted into the cell through the curved wall and was brought to a focus in a fairly small pencil inside the cell. Observations were made with the microscope *M* in Figure 2, suspended on the carriage directly above the cell. This microscope consisted of the vertical tube made of Bakelite for thermal insulation, an objective with a focal length of 16 mm immersed in the water of the trough, and a hyperplane eyepiece containing a scale divided into squares, one of

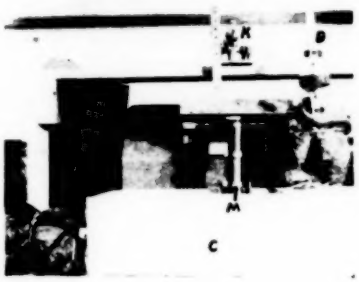

Fig. 2.

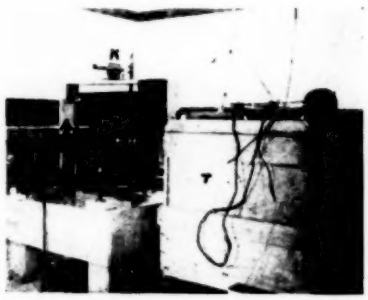

Fig. 3.

which was divided into smaller squares. The focal plane of the microscope fell within the pencil of light inside the cell and counts of the numbers of colloids inside squares could be made. Various levels in the cell could be observed by raising or lowering the entire carriage by means of four screws upon which were mounted divided heads. Two of these screws *S* can be seen in Figure 3. Large changes in height could be read from the screw-heads while small changes could be read by means of the cathetometer *K*.

Gold sols were prepared by the Zsigmondy nuclear method,[8] which was used by Westgren and is perhaps the most highly recommended for obtaining particles closely uniform in size. The La Place-Einstein law is, of course, valid only for particles having a definite radius and a definite mass. The nuclear sol was formed by the reduction of gold chloride by phosphorus dissolved in ethyl alcohol. The nuclei were enlarged in two steps by the reduction of gold chloride upon the particles by means of hydrogen peroxide (30 percent). The sol upon which observations were made was obtained by diluting this gold sol. In this preparation, it was highly important to obtain water low in both sus-

[8] Rinde, Diss. Upsala, p. 25 (1928).

pended matter and electrolyte content. A special still was constructed which employed the partial condensation of steam from water treated with potassium permanganate and potassium carbonate. The steam was passed through a settling chamber and a tin condensation tube. The water was collected in a Jena glass bottle.

Results

We shall show distribution curves for two different sols which contained particles approximately the same size, but were different in initial concentration. The temperature control for the more dilute sol was not as good all of the time as might have been desired. Also, one or two small bubbles were observed in the top of the cell when it was removed. However, the consistency of

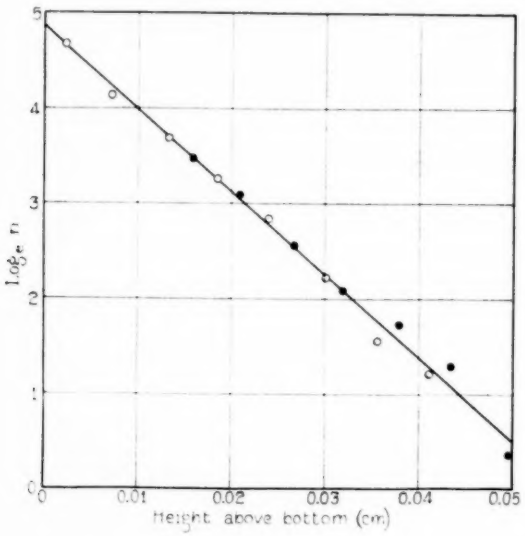

Fig. 4.

the results would indicate that no serious disturbances were set up, as one may see in Figure 4 where logarithms of concentration values are plotted as ordinates, and in Figure 5 where the same concentration values are plotted in the ordinate direction. Each of the points shown is taken from 50 counts with the exception of the two lowest points marked with circles which are taken from 25 counts. The points marked with dots were taken after about 3 days of sedimentation while the points marked with circles were taken from the same sol after about 5 days. The concentration at the end of 5 days in the upper regions was roughly one-half percent of the highest concentration observed. Such a value is even lower than the lowest point shown, so that the distribution curve lies very close to the zero axis in the upper part of the cell. This portion of the curve was somewhat higher as observed at the end of three days of sedimentation, the concentration near the top being almost as great as that shown by the lowest point plotted and also being greater than the concentration in an intermediate region. This latter would indicate that there might

have been a slight disturbance in the upper regions which was of practically no consequence in the immediate neighborhood of the bottom, where, after all, the bulk of the particles in which one is interested was located. The impor-

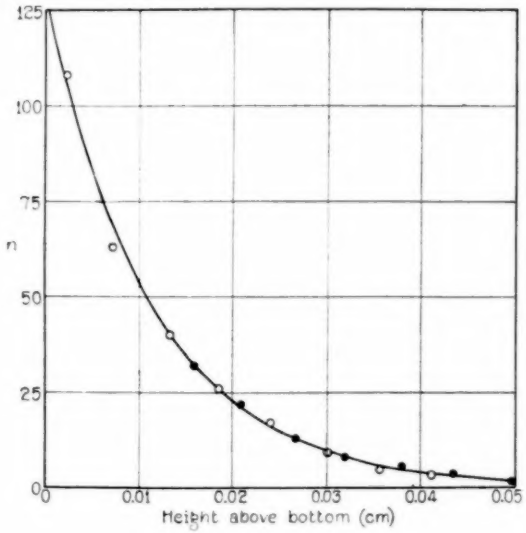

Fig. 5.

tant fact is that a steady state was reached and the distribution of the particles in this state was exponential. The slope of the curve shown in Figure 4 is 87; the temperature was 26.5°C.

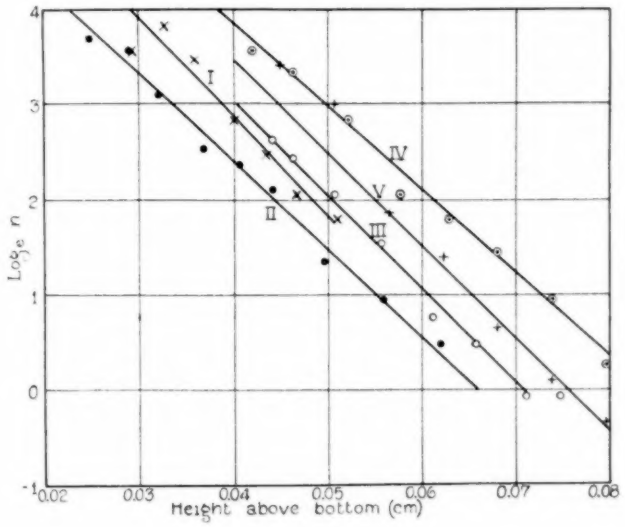

Fig. 6.

The second sol which was of higher concentration was unusually stable and the cell was allowed to remain in the thermostat for a period of about two

weeks. During the first three days of sedimentation, the two extreme temperatures observed differed by only 0.005°C, so that for long periods of time, the temperature was scarcely seen to vary on the Beckmann thermometer. The temperature was maintained at 26.5°C. Curves I to V shown in Figure 6 were obtained after sedimentation periods of 3, 5, 8, 9, and 10 days respectively. At each level marked by a point, a total of 50 counts was taken. It should be mentioned that the counts were made with quite a little difficulty due to the scattering of light near the bottom of the cell (in a large measure from the dense layer of colloids), the shifting of the light pencil due to changes of the arc, and the psychological factor attendant with such counts. However, the slopes of the curves are fairly consistent and the average is 96. The relative displacements of the curves were perhaps in a large measure due to the experimental error in locating the bottom with respect to the points, although it is not certain that actual shifts of the distribution did not occur. Certainly, it is more difficult to avoid slight disturbances in the regions observed in Figure 6 than those in Figure 4 since these regions are further removed from the damping surface at the bottom. In any case, whether the displacements were real or not, the effect was certainly of no prime importance as regards the distribution law which is seen to be exponential in character. In this solution the colloidal particles became remarkably scarce in the upper regions. On the ninth day, the concentrations observed in the main body of the sol were of the same order as those observed on the fifth day for the other sol, and thus were relatively slight since the latter sol was much the less concentrated of the two initially. This scarcity of particles is important since the distribution curve should approach the zero axis very rapidly upwards. The slight upward displacement of the experimental curve above the theoretical curve in the upper regions might be due to the lateral diffusion of particles into the cell from the side arms, the presence of particles differing in size or density from the bulk of the gold particles, and perhaps the presence of undetected slight movements of the sol.

Discussion

As has been pointed out by others, it is likely that both Burton and Porter did not take sufficient precautions against disturbing convection currents. Burton and Bishop,[9] working with copper colloids, used a large tube 94 cm long without much care in this respect. Burton and Currie,[10] working with gamboge, arsenious sulphide, Bredig copper and Bredig silver colloids, repeated the work using 145 cm tubes immersed almost completely in a thermally insulated bath. They state that this bath was stirred "from time to time" and that the temperature of the room varied slowly over a range of 7°C during the period of four months of sedimentation. It is very doubtful if such conditions were satisfactory. Porter and Hedges[11] working with gamboge particles, fractionally centrifuged to obtain uniformity in size, reported that

[9] Reference 3.
[10] Reference 3.
[11] Reference 4.

although the distribution was uniform in the greater portion of their cell's height, the concentration diminished near the top as the top was approached. We, also, found a similar distribution in our early work when there were disturbing currents. In addition, however, we found an increase in concentration near the bottom. It is unfortunate that Porter did not investigate the region in the immediate neighborhood of the bottom, although it is quite surprising he found no appreciable increase in concentration in the lowest level he reached. Barkas[12] working under Porter stated that convection currents were quite a disturbing factor in his work. It is very easily seen how there could be a settling of particles in the neighborhood of a surface even though convection currents were stirring up the particles in the central portion of the sol since the frictional drag at the surface would prevent appreciable currents from being set in motion in that neighborhood. Thus one might expect to find the diminishing concentration near the top.

Then there is the phase of the problem which concerns the time necessary for sedimentation equilibrium to be attained. The theoretical work on sedimentation has been done by Mason and Weaver[13] and Fürth.[14] Weaver[15] laid down the general rule that equilibrium should be attained within the time that it takes a particle to settle twice the depth of the cell according to Stokes' law. Later Fürth[16] stated more rigorously that the necessary time is proportional to the cell depth when RT/NXl is large, and proportional to the square of the cell depth when this quantity is small. In this expression, which is called α by Mason and Weaver, X is the resultant gravitational force acting on the particle and l is the cell depth. Fürth estimated that it would take a number of years for equilibrium to be attained in Burton's work. As already stated, the time of sedimentation was only four months. It must be mentioned that the whole problem in Burton's case is very indefinite since he did not use particles of uniform size. As pointed out by others, since Porter does not state the length of time allowed for sedimentation, it is quite possible that he did not wait long enough for equilibrium conditions. Fürth pointed out the similarity between Porter's curve and the theoretical transient state curve. In our work, we have calculated the time necessary for a gold particle to settle twice the height of the cell for the sol of Figure 4, taking the slope of the equilibrium curve to be 87. The value of the radius obtained from the La Place-Einstein equation is 3.6×10^{-6} cm. From Stokes' law, the time of settling a distance of twice our cell depth, or 1.66 cm is 76 hours or about three days. A steady state was apparently reached in our work in about 3 to 5 days. Thus, it seems that the Weaver rule holds roughly in our case. Our value of α is 0.014.

Burton[17] explained the uniform distribution curve by assuming that the colloidal particles are electrically charged and repel each other. Porter

[12] Barkas, Trans. Far. Soc. **21,** 66 (1925).
[13] Mason and Weaver, Phys. Rev. **23,** 412 (1924).
[14] Fürth, Zeits. f. Phys. **40,** 351 (1927).
[15] Weaver, Phys. Rev. **27,** 499 (1926).
[16] Fürth, Zeits. f. Physik **45,** 83 (1927).
[17] Burton, "The Physical Properties of Colloidal Solutions," p. 87.

criticised this theory by stating that the particles would tend to move to the walls of the containing vessel in such a case.

Burton[18] also suggested that the settling of colloids may be prevented by Bownian movement and defined as the "critical radius," that radius for which the particle is displaced by Brownian movement in one second the same distance through which it would fall in one second according to Stokes' law. Particles with radii smaller than this so-called critical radius would remain in suspension without sedimentation. Now, of course, as Kraemer has pointed out, Brownian movement takes place in no favored direction and it is obvious from our results that settling did take place. The critical radius of gold is several times our radius since Burton gives 28×10^{-6} cm as the critical radius of platinum, which is heavier than gold.

Porter has suggested that his results were due to the fact that his sol was no longer dilute. His concentration of gamboge particles was of the order of 10^7 per cc. From our work, the concentration represented by the highest point plotted in Figure 5 is of the order of 4×10^8 per cc. Porter's value of concentration seems far too low to justify his assumption of a concentrated sol, especially in comparison with the concentrations used by the earlier workers.

Porter has also suggested that there are three distinctive regions in a colloidal solution: the Gibbs layer located very close to the surface, the "Perrin layer" in which the colloids are distributed exponentially in a layer a fraction of a mm in thickness near the top of the vessel, and finally "a layer of one or two millimeters' thickness (in the particular cases studied in this paper), in which a further change of concentration occurs which can not be calculated in the way adopted by Perrin." The third region is close above the principal part of the sol in which the concentration is constant. From our results, we have concluded that in the case of particles more dense than water in deep cells the particles are distributed in a "Perrin layer" extending from the bottom upwards. Whether this layer extends appreciably up through the main body of the sol should depend upon the height of the vessel, the radius and the density of the particles, and the initial concentration of the particles. Certainly if one should look for an anomaly in the distribution law due to high concentration, the logical region to investigate is that near the bottom of the cell where high concentrations may be obtained. In fact Constantin[19] working with high concentrations of gamboge particles found a deviation from the exponential law in the lower portion of the range which he investigated.

In conclusion, it seems that the work on colloidal suspensions leading to a uniform distribution was very likely not free from spurious effects and that there is no change in distribution law in increasing the height of a cell. Such a conclusion is certainly in harmony with the bulk of the other work related to this phase of the study of colloidal particles.

We wish to express our gratitude to the American Petroleum Institute for the funds furnished for this research, to Dr. R. A. Millikan for his interest as director of this project, to Mr. A. A. Grubb for his aid in the experimental work and to Dr. M. E. Nordberg for constructing the quartz cells.

[18] Burton, Alexander's "Colloid Chemistry," Vol. I, p. 165.

[19] Constantin, Comptes Rendus **158,** 1171 (1914).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Inhomogeneities in Crystals (A Reply)

Dr. R. H. Canfield[1] has published in a letter of the above title some objections to my theory of the mosaic structure of crystals. His arguments are based on a very serious misunderstanding of my considerations.[2] In order to clear up the case, I shall repeat here the general method which enabled me to find configurations of lower energy than that of the crystallographically ideal crystal. For the sake of an unambiguous illustration, I shall give the energy changes involved for the very specific case of an NaCl crystal.

Using the notations of loc. cit., we have $d_0=5.6$A for the lattice constant of NaCl. The lattice constant of an isolated (100) plane "in equilibrium," which is not sandwiched in between other (100) planes, is $d=0.94d_0$. The outline of my method for finding the configurations of low energy given in loc. cit. p. 818 is literally this.

"α) Contract (an arbitrary plane 100) II so that its spacing is changed from d_0 to d.

β) Fill the gaps which have been opened by α between the two remaining parts I and II of the crystal.

γ) Rearrange the relative position of I and II in a certain way."

If we disregard the polarizability of the atoms for a moment, then the process α involves an energy change $\epsilon_\alpha=\epsilon_1+\epsilon_2$, where ϵ_1 represents the (negative) energy of contraction of the plane II under its own forces. ϵ_2 is the positive energy which has to be supplied in order to annihilate the energy of the plane II relative to the remaining parts I and II. It is easily seen that ϵ_2 if taken per cm^2 is approximately equal to $2\sigma=300$ ergs where σ is the theoretically derived surface energy of NaCl. The value for $\epsilon_1\leqq-220$ ergs/cm^2 may be obtained from curves published by I. E. Lennard-Jones and B. M. Dent[3] for instance. It is $\epsilon_1+\epsilon_2>0$ as Mr. Canfield justly remarks. Otherwise an NaCl crystal would fall apart.

The step β involves a negative energy change which is easily seen to be 12 percent of 2σ approximately. This yields $\epsilon_3\leqq-36$ ergs/cm^2. The rearrangement γ in our specific case is a very simple process. Exchange all the positive ions with all the negative ions in part I of the crystal. This leaves the relative energy between I and the plane II unaltered. It involves, however, a small negative change of energy of I relative to II; namely, $\epsilon_3\leqq-20$ ergs/cm^2.

Finally, we have to consider the polarizability of the ions. In the ideal crystallographic configuration, the ions are in locations where the electric field strength is zero. The ions (e) of our II plane, however, are subjected to fields of the order of $E=4e/d_0^2$ e.s.u. due to the rearrangement γ of the relative position of I and II. We therefore have lowered in this way, the energy of an ion in the II-plane by an amount $|\delta\epsilon_4|=\alpha E^2/2=8\alpha e^2/d_0^4$ where α is the polarizability of the ion. The average value of α for the couple Na^+ and Cl^- may be taken equal to that of Ne and A with sufficient accuracy. This results in $\alpha=10^{-24}$ cm^3. We therefore obtain $\delta\epsilon_4=-1.8\times10^{-13}$ ergs/cm^2. As there are $n=1.3\times10^{15}$ ions per cm^2, we have $\epsilon_4=n\delta\epsilon_4=-230$ ergs/cm^2. This value has in reality to be multiplied by a factor of the order of three, because of the fact that the ions in the two neighboring planes of II are also subjected

[1] R. H. Canfield, Phys. Rev. **35,** 114 (1930).

[2] F. Zwicky, Proc. Nat. Acad. Sci. **15,** 816 (1929). Will be referred to as loc. cit.

[3] I. E. Lennard-Jones & B. M. Dent, Proc. Roy. Soc. **A121,** 259 (1928).

to the same high fields. In any case the, figures show conclusively that the total change in energy is $\epsilon=\epsilon_\alpha+\epsilon_\beta+\epsilon_3+\epsilon_4<0$ which verifies my general contention for the case of rock-salt.

The principle which led me to the conception of the mosaic structure might be called the *principle of the slight asymmetries in complex configuration* such as atoms, molecules, and crystals. *Indeed, due to the deformability of the atoms and molecules, nature, according to the above, definitely favors configurations which are somewhat asymmetrical.* I owe to Professor O. Stern the remark that this principle might apply to cases like $H_2O=(HO^-+H^+)$.

The trivial consideration mentioned by Mr. Canfield that under the proper circumstances, certain planes like (111) have a tendency to expand has not escaped my attention. Indeed, I have thought out its consequences long ago. One of them I have mentioned, loc. cit. p. 820, "In regard to the space groups characterizing the primary and the secondary (mosaic) structure, it must be remarked that they are not necessarily the same, etc."

In regard to the experimental evidence which we have secured so far, I can mention here only that it supports my conception of a *spacial* mosaic structure. It is not a surface phenomenon only as Mr. Canfield seems to think. Moreover, if an indirect argument is wanted, I may mention the quantitative agreement which can be obtained on the basis of my theory with some of the important phenomena related to the *slipping strength* (not the tensile strength). For all further detailed information, I have to refer the reader to several articles by my collaborators and myself which will be published presently. A complete representation of my theory is now in preparation for the Helvetica Physica Acta.

Finally, I wish to make a remark in regard to the development of the theory. Mr. Canfield intimates that I had secured direct experimental (optical) evidence for the mosaic structure first, and then developed a theory "resulting in a prediction of the required phenomenon." I can only state that the exact contrary is true, inasmuch as *all* the experimental investigations at this Institute dealing with the mosaic structure have been undertaken at my suggestion to check the theoretical predictions and *all* the evidence obtained is posterior to the development of the essentials of the theory.

F. ZWICKY
Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena, California,
January 23, 1930.

The Effect of Dilution upon the Raman Spectra of Nitric Acid

Photographs of the Raman spectra of dilute and concentrated solutions of nitric acid in water obtained in this laboratory last May show striking differences in the frequencies of the lines scattered in the two cases. Lines which are strong in commercial 70 percent acid become weak and ultimately disappear as the acid is diluted, and other lines, weak in the concentrated acid grow strong, reach a maximum intensity and disappear as the dilution becomes infinite. In a recent note to Nature (**124,** 762 (1929)) I. R. Rao reports similar results. As Rao points out, the effect can be attributed to dissociation. The lines which are strong in the concentrated acid and which disappear upon dilution are very probably due to the HNO_3 molecule. Those which are greatly enhanced by dilution can be attributed to the NO^-_3 ion.

Four infra-red frequencies, two forming a doublet, give rise to the strong scattering in the concentrated acid, and hence may be associated with the HNO_3 molecule. They are 618, 669, 937, and 1293 cm^{-1}. One transition, at 1034 cm^{-1}, grows enormously strong with dilution, reaching its greatest strength, approximately, in mixtures of equal volumes of water and commercial acid. Rao attributes the doublet at 618 and 669 cm^{-1} (given by him as 630 and 689 cm^{-1}) to the NO^-_3 ion. On the plates obtained by the author this pair behave exactly as do 937 and 1293 cm^{-1} disappearing completely in a 25 percent solution of the commercial acid. At this dilution 1034 cm^{-1} is still of high intensity. Rao reports, in addition, a Raman frequency at 3319 cm^{-1} and attributes it to the HNO_3 molecule. No such frequency was found on the present plates. The doublet transition 618 and 669 cm^{-1} which is strongly excited by the mercury line 4358 appears only feebly excited by 4046 in concentrated acid. An

interpretation of this as a singlet transition excited by the 3650 mercury line would give a scattering frequency of 3328 cm^{-1}. It is possible that this corresponds with Rao's reported 3319 cm^{-1} transition which he attributed to the HNO_3 molecule.

The variation of the intensity of the lines with dilution is clear cut and is believed to be the second optical indication of the formation of different molecular or ionic species by the dilution of strong acids. The first was obtained years ago by Pfund (Astrophys. J. **24,** 19 (1906)), who observed differences in the infra-red frequencies, reflected from surfaces of fuming and dilute sulphuric acid. The effect undoubtedly affords a new probe into the processes of dissociation in solution and will be particularly useful in cases where the strong absorption of water makes the solution opaque to the infra-red. The Raman work is being extended to salts, other acids and electrolytes, and in collaboration with Professor Ellis the infra-red absorption spectra, as a function of concentration, are being studied.

E. L. KINSEY

University of California at Los Angeles,
Los Angeles, California,
January 16, 1930.

Note on Electron Scattering in Atomic and Molecular Hydrogen

The theoretical scattering formula in the paper on Electron Scattering in Atomic and Molecular Hydrogen in the Physical Review of September 1st, 1929, refers to the number of electrons scattered between the angles θ and $\theta+d\theta$, whereas the experimental points represent the scattering in the solid angle between θ and $\theta+d\theta$. In order to make the experimental points refer to the quantity given by the theoretical formula they must be divided by a factor proportional to the sine of θ. When this is done to the results for inelastic scattering the points are in much better agreement with the theoretical curve. But when the proper correction is applied to the results for elastic scattering the agreement with the theoretical curve is not as good as that given in the paper. The departure from the curve at small angles is probably due to the influence of adsorbed gas on the slits of the apparatus. Some evidence of this was found during the experimental work but it was not a factor which could be accurately determined and corrected for. It would be of about the right amount to account for the observed departure at small angles. At large angles the observed scattering would differ from that predicted by the formula. The explanation of this effect is not clear, unless it is due to the scattering from molecular hydrogen. It is hoped to obtain further information on these points with an apparatus of different design.

GAYLORD P. HARNWELL

Princeton University,
January 14, 1930.

Evidence of the Presence of Element 87 in Samples of Pollucite and Lepidolite Ores

Element 87 is peculiarly well placed in the periodic table for detection by a new and very sensitive method recently reported by us. (Phys. Rev. **35,** 124 (1930).) We have accordingly made a search for this element in samples of pollucite and lepidolite ores supplied by the Research Laboratory of the General Electric Company, and we have consistently found minima at points of the scale which correspond to an element of the atomic weight and the valence ascribed to eka-caesium. We have studied the substance in the chloride, sulphate, nitrate and hydroxide compounds, in each case finding the minima at points of the scale characteristic of an element of the chemical equivalent of eka-caesium. Since the same element in different compounds produces its characteristic minima of light at different points of the scale, the fact that minima are observed in each of the four compounds at the points appropriate to element 87 affords evidence of considerable weight for its presence in the sample under test. The element appears to have several isotopes, as judged by the number of its characteristic minima. The method employed is sufficiently delicate to detect less than one part of a compound in 10^{10} parts of water. The work is still in progress.

FRED ALLISON
EDGAR J. MURPHY

Department of Physics,
Alabama Polytechnic Institute,
January 11, 1930.

Voltage Intensity of λ2537 in Mercury

In a recent paper (Phys. Rev. **34,** 1352 (1929)) note was made that the curve (Fig. 3) showing the relation between the voltage of the electrons and the intensity of the radiation from mercury vapor apparently was a composite of two curves, one with a maximum at about 5.5 volts and the other with a maximum at about 5.95 volts. Since the whole radiation from the beam was focused on the photographic plate it was not possible to decide whether these two maxima are characteristic of λ2537 alone or whether at about 5.7 volts a new radiation, possibly a molecular band, was added to λ2537. In this connection it was thought significant that in critical potential measurements under similar conditions a critical potential at 5.7 volts is always found.

The purpose of the present letter is to present results which indicate that the curve given in the paper referred to is characteristic of λ2537 alone, and that no light of other wave-length is responsible for the appearance of two maxima in that curve.

The light from the excitation tube was passed through a 2.9 cm path of a solution of 1 part of glacial acetic acid to 200 parts distilled water. This cell absorbed about 95 percent or more of light of wave-length shorter than 2350A and about 75 percent of light of wave-length 2537A. This would decrease any light of wave-length less than 2350A to $\frac{1}{4}$ or less of its former relative importance. A curve was taken with the cell in place and it checked the two previous runs as closely as they checked each other. This indicated that there was no appreciable amount of light of wave-length less than 2350 affecting the photographic plate.

A spectrograph was made of a monochromatic illuminator. The slit of the illuminator was removed and the beam of light from the tube was used as a slit. A special ultra-violet plate made by the Eastman Kodak Company was used to emphasize any light in this wave-length region, but no light was found other than λ2537.

FLOYD C. OSTENSEN
University of Minnesota,
January 20, 1930.

BOOK REVIEWS

Advanced Laboratory Practice in Electricity and Magnetism. EARLE M. TERRY. Second Edition, 1929. Pp. 318, figs. 175. McGraw-Hill Book Co., New York. Price $3.00.

This is a second and somewhat larger edition of Professor Terry's well-known manual for use in a course which in many institutions is called "Electrical Measurements." The introduction a dozen or so years ago of the use of audiofrequency oscillatory currents into laboratory experiments and the development of very sensitive telephone receivers revolutionized the methods (and the theory) of the measurement of capacitance, and self and mutual inductance. The first edition of this book was outstanding in its use of these newer methods. In the new edition the number of experiments has been increased by about 25 percent, most of the new ones being on three-element vacuum tubes and oscillatory circuits. These new experiments have been so planned that they may be used in a course on radio communication. The extensive use of vacuum tubes in many types of physical measurements makes it desirable to give in our advanced laboratory courses experiments in this field. The same clearness that was characteristic of the presentation of both the theoretical and the experimental parts of the first edition is shown in the additions.

The manuscript for this edition was finished by Professor Terry before his death and the responsibilities connected with the publication were undertaken by Professor H. B. Wahlin, a colleague in the University of Wisconsin.

O. M. STEWART

The Electromagnetic Field. MAX MASON AND WARREN WEAVER. Pp. xiii+390. University of Chicago Press, 1929. Price $6.00.

In his attempt not to discourage the student with lengthy analysis and fine reasoning the author of the average text on electromagnetism glosses over many delicate logical difficulties in a way that often proves very disturbing to the thoughtful reader. The authors of the present volume, on the other hand, have attempted to present the fundamentals of the classical electromagnetic theory with as great a degree of mathematical rigor as the subject permits, and have been exceptionally successful in achieving their objective. Their argument requires in many places the closest attention on the part of the reader, but any effort on his part is well repaid by the very much clearer understanding of the subject which he gains. The treatment is necessarily quite mathematical, and the close analysis of the subject which the authors have undertaken has necessitated a rather annoying recourse to subscripts and accents. The book is hardly one which can be recommended as an introductory text in electromagnetism but to the advanced student who is looking for a rigorous development and critical study of the subject it should prove invaluable.

The very elegant treatment of the difficult subject of dielectrics in electrostatic fields merits particular commendation. In so far as the potential theory aspect is concerned it leaves little to be desired. On the other hand the equally difficult subject of stresses in dielectrics and on conducting surfaces, which is perhaps more puzzling to the student than any other part of electrostatics, has hardly received an adequate presentation.

The authors make no attempt to develop the relation between electrodynamics and the special relativity theory, nor do they make any use of four-dimensional vector analysis. Instead of the significant three-dimensional vector notation of Gibbs they have preferred to use the parentheses, brackets, divs and curls which European writers generally employ. They have been careful to avoid any mention of lines of force either electric or magnetic, a procedure which can hardly be claimed to increase rigor while it deprives the reader of the aid of a convenient geometrical picture. A feature much to be commended is the placing of an introduction at the beginning of each part of each chapter and of a concluding paragraph at the end. In this way the reader is given an idea of the aim of each part before he enters upon

the analytical details and he gains from the conclusion at the end a perspective which he might otherwise miss.

The book is divided into four chapters each of which contains several parts. The titles of the chapters are "Coulomb's Law and Some Analytic Consequences," "The Electrostatic Problem for Conductors and Dielectrics," "Magnetostatics" and "The Maxwell Field Equations." In addition to the formulation of Maxwell's equations the last chapter takes up the activity equation, electromagnetic waves, retarded potentials, and the concept of electromagnetic mass. The discussion of the activity or energy equation is especially clear and searching. At the end of the book are a mathematical appendix on vector analysis, a formula index and a general index.

While the book contains much analysis the physics of the subject is by no means neglected and every difficult point is carefully and fully explained. The process of averaging in the case of a dielectric, for instance, is discussed in much detail with illustrations drawn from outside the subject of electromagnetism. The whole work gives every evidence of the most careful and painstaking preparation. It constitutes unquestionably the foremost critical study of electromagnetic theory in the English language.

LEIGH PAGE

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE DES MOINES MEETING, DECEMBER 30 AND 31, 1929

The Thirty-first Annual Meeting (the 161st regular meeting) of the American Physical Society was held in Des Moines, Iowa at the Hotel Fort Des Moines on Monday and Tuesday, December 30–31, 1929. The presiding officers were Professor Henry G. Gale, President of the Society, and Professor P. W. Bridgman. The average attendance was about 150.

On Tuesday morning Professor Henry G. Gale delivered the presidential address, his subject being, "The Interplay between Theory and Experiment in Modern Spectroscopy."

The annual joint session with Section B was held on Tuesday afternoon. The presiding officer was Professor Charles E. Mendenhall, Vice-President of Section B. The program consisted of the address of the Retiring Vice-President of Section B, Professor P. W. Bridgman, on the subject, "Permanent Elements in the Flux of Present Day Physics." In addition there were two invited papers, "Polarization of Matter Waves" by A. Landé, University of Tübingen (Germany), (Ohio State University 1929–1930) and "The Wave Mechanics of Collision Processes" by L. H. Thomas, University of Cambridge (England), (Ohio State University, 1929–1930).

On Monday evening, December 30, there was a dinner for the members of the Society and Section B and their friends in the Hotel Fort Des Moines, attended by seventy-five persons.

Annual Business Meeting. The regular annual business meeting of the American Physical Society was held on Tuesday afternoon, December 31, 1929 at three o'clock. A canvass of the ballots for officers resulted in elections for the year 1930 as follows:

President:	Henry G. Gale
Vice-President:	W. F. G. Swann
Secretary:	W. L. Severinghaus
Treasurer:	George B. Pegram
Members of the Council, Four year term:	L. W. McKeehan D. L. Webster
Members of the Board of the Physical Review, Three year term:	F. W. Loomis K. F. Herzfeld A. W. Hull

The Secretary reported that during the year there had been 261 elections to membership. The deaths of 4 members had been reported during the

year; 30 had resigned and 38 had been dropped. The membership of the Society as of December 31, 1929 was as follows: Members: 1834; Fellows: 532; Honorary Members: 6; Total Membership: 2372. The numbers are approximate because they include elections and transfers at the November and December meetings. In the year there had been a net increase of 197 members and a net increase of 12 fellows.

The Treasurer's financial report for the year 1929 was presented by the Secretary.

The Managing Editor presented the financial report for the Physical Review for the year 1929 and for the Physical Review Supplement for May 1, 1929 to November 30, 1929. The reception of the Supplement by the members of the Society and others was reported to be very gratifying. A greatly increased speed of publication of papers and letters for the Physical Review was also reported. The number of pages printed increased over last year as did also the cost per page of printing. An operating loss of approximately $2400 in the publication of the Physical Review for 1929 was reported.

At this session the Council announced that in the week of June 16th the Society would hold a meeting at Ithaca, New York, by invitation from Cornell University. This meeting is to be of a somewhat less formal nature affording more time for discussion of the papers presented.

Meeting of the Council: At its meeting held on Monday morning, December 30, 1929, six persons were elected to fellowship, five were transferred from membership to fellowship and forty-six were elected to membership. *Elected to Fellowship:* Robert d'E. Atkinson, James A. Beattie, Edward Mack Jr., Thomas H. Osgood, Hugh S. Taylor, and J. W. Williams. *Transferred from Membership to Fellowship:* Gaylord P. Harnwell, Robert B. Lindsay, Harry B. Maris, Jonas B. Nathanson and E. P. T. Tyndall. *Elected to Membership:* Homer G. Anderson, Soichiro Asao, Robert F. Bacher, James W. Ballard, Fred J. Beck Jr., Lowell C. Beers, Claud E. Cleeton, Howard L. Cobb, Samuel G. Cook, William F. Drea, Charles Foster, Darol K. Froman, Willard Geer, Yu Ming Hsieh, Hugh H. Hyman, Ellis A. Johnson, Matthew T. Jones, E. B. Jordan Jr., Walter H. Jordan, Louis S. Kassel, Ray W. Kenworthy, P. W. Ketchum, Jackson G. Kuhn, Frances M. Lemery, John A. Madigan, Kyuzi Matukawa, Iwao Miyake, Lawrence D. Montgomery, Herbert D. Owens, Everett R. Phelps, L. R. Philpott, Robert M. Pinkerton, Cyrus A. Poole, G. W. Presnell, W. R. Pyle, Bernhard A. Rose, Herman M. Roth, Otto Rothenstein, L. A. Sanderman, H. W. B. Skinner, Masamichi So, Roy R. Sullivan, Hisao Suzuki, Ryozo Tajime, Vernon Thornton and Tameiti Yasaki.

The regular program of the American Physical Society consisted of 32 papers. Numbers 4, 9, 16, 18, 19, 20, 22, 24, 26 and 28 were read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

W. L. SEVERINGHAUS, *Secretary.*

ABSTRACTS

1. X-ray scattering by mixtures of organic liquids. A. WESLEY MEYER, *University of Iowa.*—The x-ray scattering curves for the following mixtures were obtained; n-ethyl alcohol—methyl cyclohexane, *n*-butyl alcohol—orthodimethylcyclohexane, quinoline-phenol, cyclo-hexane—tetranitromethane and phenol-water. All mixtures but the last one are totally miscible, and it is a solution with either large water content or high phenol content but is an emulsion at other concentrations, but may be dissolved by heating. The resulting curves have peaks to which Bragg's Law is applied to obtain the spacings of the molecules in the cybotactic groups. The results indicate that in every case of solution there is a single type of cybotatic group in which both kinds of molecules participate. The molecular spacing of the group is intermediate between the spacings of the pure liquids and dependent upon the number of each kind of molecule present. In the phenol-water emulsion curves, two spacings were found corresponding to those of saturate phenol water, and saturate water phenol, agreeing with the common belief that the molecules of the constituents of an emulsion do not intermingle, except in large groups, the constituents in this case being the two saturate solutions. The conclusion concerning solutions agrees with that obtained in cases of solid solutions such as alloys.

2. Dependence of viscosity in liquids upon the molecular space arrangement as shown by x-ray diffraction. R. L. EDWARDS, *Miami University* and G. W. STEWART, *University of Iowa.*—It has become possible to make a comparison between the physical condition of a liquid and its viscosity. Twenty-one octyl alcohols made under the direction of Professor E. Emmet Reid of Johns Hopkins were examined by x-rays. The "perfection" of the molecular groups were estimated by the magnitude of the secondary diffraction peaks which evidently depend upon the planar spacing of diffraction centers in the direction of the length of the molecules rather than diametrically. The coefficients of viscosity were obtained by the measurements of Professor E. C. Bingham of Lafayette College. When the OH group is in a fixed position and a methyl group of the octyl alcohol is placed in the possible positions in the molecule, the variation in the coefficient of viscosity varies in a manner similar to that of the magnitude of the secondary peak. The agreement is striking because the variations are large. The interpretation made is in accord with the obvious effects that grouping of molecules to any extent would have. The need of the incorporation of the cybotactic condition or molecular grouping in any theory of viscosity of liquids is emphasized.

3. The extent of noticeable cybotactic condition in a liquid as exhibited by triphenolmethane. G. W. STEWART, *University of Iowa.*—By means of the comparison of the chief x-ray diffraction peak of triphenolmethane in powdered crystal form with that occurring with the liquid, an approximate estimate may be made of the extent of the condition of molecular space grouping throughout the liquid. Areas of the diffraction curves were determined, the experiments being made with thicknesses of material, equal as determined by weight. It was found that the total diffracted energy in the chief diffraction peak of the first order was greater with the liquid than the crystal. Properly interpreted this means that the effective groupings of the molecules in the liquid are approximately of the same extent in the liquid as in a finely powdered crystal. Ignorance concerning the exact nature of the grouping and the structure factors prevent any quantitative comparison.

4. The structure of certain *K* series emission lines. J. VALASEK, *University of Minnesota.*—Recently, Davis and Purks have reported several new satellites near the $K\alpha_1$ and α_2 emission lines of Ni, Cu, and Mo, and $K\beta_1$ of Mo, using a double-crystal spectrometer. The writer has attempted to confirm these results in Siegbahn's laboratory, using a new single-crystal spectrometer designed by Siegbahn. With the slit 0.03 mm wide and the plate at 3 meters, the resolving power in the first order was equal to that of the double-crystal spectrometer in the first order. According to the curves given by Purks, some of the satellites should be perceptible in the first order. Microphotograms were made of the following lines: $K\alpha_1$ and α_2 of Cu, Mo, and Ag, and $K\beta_1$ of Mo. No satellites were found. Lack of time prevented observations in the second order.

5. Fine structure in *K* x-ray absorption spectra. BEN KIEVIT, JR. and GEO. A. LINDSAY *University of Michigan.*—The *K* x-ray absorption spectra of the free elements Ca, Cr, Mn, Co, Ni, Cu and Zn have been photographed and for each of these elements an extended fine structure has been obtained. This fine structure, consisting of six or seven secondary edges, extends over an energy range of some 200 volts. In every instance the element was used as the absorbing screen except in the case of manganese where it was present in the alloy manganin. Indications are that the alloy screen gives the same result as the element alone. A KCl crystal served as reflector to obtain the spectra. Additional exposures were made with copper and with zinc, using the [111] face of calcite as reflector in order to increase the dispersion in this region of shorter wave-lengths. An attempt is made to account for the observed phenomenon on the basis of multiple ionization. The atom absorbs energy sufficient to remove a *K* electron to the first permissible unoccupied orbit and also to eject an outer electron. One is led to the conclusion that probably similar fine structure might be obtained for all elements under suitable conditions.

6. The intensity of reflection of the Kα line of carbon from a quartz surface. ELMER DERSHEM AND MARCEL SCHEIN, *University of Chicago.*—The $K\alpha$ line of carbon ($\lambda = 44.6$A) was reflected from a polished quartz surface and the intensity of the reflected radiation measured for glancing angles of incidence between 1° 15′ and 8°. The apparatus and methods have been previously described (Phys. Rev. **34**, 1015 (1929)). The curve obtained by plotting the experimental values of reflected intensity against glancing angle of incidence is compared with various curves computed from the theoretical value of the index of refraction given by the Drude-Lorentz dispersion formula and values of the absorption coefficient obtained by the extension to this long wave-length region of various well-known empirical formulas relating to x-ray absorption. A calculated curve which is in good agreement with the experimental curve may be secured by the use of a mean of the values of the absorption coefficient for this wave-length in quartz which are given by the different empirical formulas.

7. An x-ray search for the origin of ferro-magnetism. J. C. STEARNS, *University of Denver.*—A sensitive null method, employing two crystals and two ionization chambers, was used to detect any change in the intensity of the Molybdenum K_α reflected from a magnetic crystal when this crystal was magnetized. This method was capable of detecting from 1.0 to 0.1 percent change in the intensity, according to the intensity of the reflected beam. Crystals of magnetite and silicon were used. The change in the intensity of the x-ray beam was computed on the basis of the alteration of the structure factor due to the orientation of the electronic orbits by the magnetic field. The experimental results indicate that there is no change in the reflecting power of crystals of magnetite or silicon steel due to magnetization. It is concluded that electrons revolving in inner orbits within the atom cannot account for ferromagnetism. On the basis of present atomic models and present experimental evidence it appears that the ultimate magnet should be identified with the spinning electron.

8. Magnetic properties of thin films of cobalt. E. P. T. TYNDALL AND W. W. WERTZBAUGHER, *University of Iowa.*—The films are deposited elytrolytically on brass tubes from a 3% solution of cobalt ammonium sulphate with the addition of boric acid. The magnetic properties are largely dependent on the amount of boric acid present in the solution. Films deposited from solutions nearly saturated with boric acid show almost complete magnetic saturation at $H = 200$ gauss ($I_{max} = 1300$ c.g.s. units) and have very high remanence, about 98% of the maximum intensity of magnetization. The reciprocal of the coercive force is roughly proportional to the film thickness for films from 30 to 130 mμ thick, in approximate agreement with the relation previously found for iron (Phys. Rev. **30**, 681 (1927)). Films from less acid solutions depart considerably from this relation. The properties of the films are undoubtedly partly due to occluded hydrogen, the effect of which is at present being investigated by heating the films.

9. Will the magnetic pole vanish? F. W. WARBURTON, *University of Oklahoma.*—By considering the parallel plate condenser and the long solenoid as sources of uniform electric

and magnetic fields respectively, the physical picture of the behavior of dielectrics and of magnetic media (in terms of displacement charge and of the equivalent magnetization current appearing at the respective surfaces) is very evident. The picture is simple and obviates the need of defining and using the fictitious magnetic unit pole even in elementary presentations. E, like B, is dependent on the medium, while D and H are the fields when dielectrics and magnetic media are absent. Non-uniform fields may be considered by the superposition of simpler cases. Were the charge on a condenser rather than the potential difference maintained constant a potential $V'=\int Dds$ would be useful as well as the ordinary potential $V=\int Eds$. Somewhat similarly a scalar magnetic potential $\phi'=\int Hds$, related to ampere-turns, is rather more useful than $\phi=\int Bds$, because it is the current in the solenoid and therefore H, not B, that is externally controlled. H and B can be derived from the corresponding vector potentials, A' and A.

10. Reflection of zinc atoms from NaCl crystals. HAROLD A. ZAHL, *University of Iowa.*—Zinc atoms issuing from a boiler at a temperature of 600°C are in part specularly reflected from a clean cleavage surface of a rock-salt crystal. Measurements, by means of a rotating sectored disc-velocity-filter, of the velocity of the specularly reflected beam show that it contains atoms of but one velocity (or at least a very limited range of velocities). This velocity varies with the angle of incidence as shown below.

θ		vel(m/sec)		Average	$\phi\times10^{14}$
22.5	763	736	761	753	4.4
45.0	666	672	683	674	12.1
67.5	712	689	695	699	22.2

An equation of the form $\lambda=h/mv=2d(1-2\phi/mv^2-\cos^2\theta)^{1/2}$ will not represent these results if ϕ is a constant. If it is assumed that ϕ varies with the angle of incidence then of course the equation may be made to fit. Values of ϕ calculated on this assumption are given in the table.

11. Specular reflection of atoms from crystals. A. ELLETT, *University of Iowa.*—The existence of specularly reflected nearly monochromatic beams of atoms and the behavior of these beams on reflection from two crystals in succession (Phys. Rev. **34,** 493, (1929)) is most readily understood as a wave or diffraction phenomenon. Neither the previous observations on cadmium nor those just reported on zinc can be represented by the equation $\lambda=h/mv=2d(1-2\phi/mv^2-\cos^2\theta)^{1/2}$ if ϕ is supposed to be constant. If it is assumed that ϕ varies with the angle of incidence and this equation used to calculate the appropriate values, we find

θ	22.5°	45°	67.5°
$\phi_{Zn}\times10^{14}$	4.4	12.1	22.2
$\phi_{Cd}\times10^{14}$	4.84	13.2	19.6

The fact that the values obtained run roughly parallel may be significant. These values of ϕ correspond to the existence of a repulsive force acting upon the impinging atom and to values of the refractive index for phase waves $\mu=[1-2\phi/(mv^2)]^{1/2}$ less than unity. Both Davisson and Germer and Farnsworth have reported dispersion of the refractive index for electron waves, but the range of variation is much less than that found here.

12. Secondary electrons from contaminated metal surfaces. PAUL L. COPELAND, *University of Iowa.*—Small quantities of grease, or gases, or foreign metal upon a metallic surface have in the past been the cause of many spurious electrical effects. Stuhlmann and Compton cite a spurious contact potential difference of some 60 volts. Using electron reflection as a tool some of the properties of such surfaces have been investigated. The presence of surface impurities on a tungsten wire greatly increases reflection or secondary emission when electrons strike the filament. Surface fields are set up retarding the reflected electron; in some cases the film actually is an insulating layer which breaks down under a potential difference of some 50 volts, which may account for the results of Stuhlmann and Compton.

13. Electron energy losses in mercury vapor. CASTLE W. FOARD, *State University of Iowa.*—An improved magnetic spectrum method was used to determine the energy losses

sustained by slow speed electrons in mercury vapor. Electron energies up to 60 volts were used, the main region of interest being from 0 to 25 volts. The energy losses detected, below that required for ionization, were; 4.9, 5.4, 6.7, 7.7, 8.8, 9.8 volts. These correspond to practically all the transitions of a valence electron from the basic 1*S* level up to each of the higher levels to 4*P*. No evidence of other losses such as are observed by the photoelectric method was found. At voltages above 10.4, the ionization potential, electrons seem to be able to give up any quantity of energy in excess of that required for ionization, the higher losses being favored. A very interesing loss of 11.07 volts has been found, which has not been recorded heretofore. It begins to be resolved at about 18 volts, and grows steadily with increasing voltage in much the same manner as the 6.7 volts loss. It is thought that this loss involves the displacement of both valence electrons from their normal levels.

14. On the electric arc drawn in vacuum. RAGNAR TANBERG, *Westinghouse Elect. Mfg. Co.* (*Introduced by J. Slepian.*)—In an electric arc drawn in vacuum, the cathode only contributes vapor to the maintenance of the arc, if the arc is of sufficiently short duration. The speed of the vapor emitted from the cathode spot is of the order of $15.\times10^5$ cm/sec. and the temperature calculated from this molecular velocity is of the order of 500,000°K. Low voltage and high voltage vacuum arc forms have been observed, depending upon the location of the cathode spot relative to the anode. The low-voltage form appears when the cathode spot is so located as to discharge the cathode vapor into the arc stream. The highly ionized cathode vapor in this case prevents the development of negative space charges which otherwise would build up. The high voltage form appears when the path of the cathode vapor does not coincide with the arc stream. Motion of the arc in a transverse magnetic field between solid metal electrodes in a direction opposite to that which would be expected from ordinary electrodynamic considerations has been observed and explained by the bending of their path by the magnetic field and subsequent impingement on the cathode surface of some of the positive ions in the cathode vapor.

15. Voltage-intensity relations of the cadmium spectra. DEVER COLSON, *University of Iowa.*—The critical potentials for different spectrum lines are given by spectrum analysis. Qualitative observations of these critical potentials have been made by Ruark and Chenault and Esclangon and have been used for the differentiation of the different orders of the spark spectra of cadmium. The present work gives more exactly the critical potentials of the more prominent arc and spark lines and traces their behavior as a function of the energy of the impacting electron. The existence of 2^3D orbits suggested but not adopetd by Von Salis is indicated.

16. Absorption of light by flames containing sodium. C. D. CHILD, *Colgate University.*—The intensity of sodium light from a series of flames into which a saturated solution of sodium chloride is sprayed was found to vary approximately as the square root of the number of flames. As the amount of sodium in the flames is diminished the ratio between the light from several flames and that from one becomes greater. These observations may be explained by assuming; first, that the number of sodium atoms in the flame which are able to emit light in a given direction or to absorb light going in that direction is very much less than the total number of sodium atoms in the flame and secondly that even this limited number is greatly diminished by the process of absorbing sodium light which is going in the direction considered. A possible explanation for these assumptions is that atoms emit light in a direction which bears a definite relation to the orientation of the atom at the time it is emitting the light and absorbs only light which is going in the same direction.

17. The use of homogeneous coordinates in physics and chemistry. HERBERT J. BRENNEN, *Northwestern University.*—It is shown that homogeneous coordinates can be advantageously used in the following cases: 1. A generalisation of the third law of thermodynamics. 2. Equations of state. 3. A generalisation of the phase rule to take account of the change of vapor pressure of a substance, at constant temperature, with the size of the particle. In order to take account of the change of vapor pressure of a substance at constant temperature with the

total pressure on the system, the phase rule may be still further generalised by the introduction of a new coordinate the total pressure on the system. 4. The restricted theory of relativity where the four planes are: $X=0$, $Y=0$, $Z=0$ and $\mathfrak{T}=0$, where $\mathfrak{T}$ is the product of the velocity of light and the time. 5. The general theory of relativity where we have four surfaces analogous to the four planes in the restricted theory. Hence, by the use of homogeneous coordinates, four dimensional relativity becomes a problem in a space of three dimensions.

18. Zodiacal light and magnetic storms. E. O. HULBURT, *Naval Research Laboratory.*—From April, 1853, to April, 1855, Rev. George Jones, U. S. N., observed the zodiacal light every night, weather and other things permitting. A comparison of his record with the Greenwich magnetic storm list gave the following results: In this period there were 26 magnetic storms, or storm groups, and 23 periods of abnormal zodiacal light, 16 of which followed within 3 days after a magnetic storm. 10 storms occurred on dates for which there were no zodiacal light observations, and there were 7 cases of abnormal zodiacal light with no accompanying magnetic storms listed. The abnormalities in the light were mainly fluctuations, and sometimes an unusual brilliance or distribution in the heavens. The correspondence between zodiacal light behavior and magnetic disturbance indicates, but does not prove, that the light comes from particles originating from the terrestrial atmosphere, in accord with the views of Barnard and others. It seems possible to sketch out a qualitative theory by considering the behavior of the high flying terrestrial ions under the influence of gravitation, light pressure and the terrestrial magnetic field.

19. Changes in the ozone concentration of the atmosphere. RICHARD RUEDY, *Toronto.*—An ozone layer equivalent to 3 mm being situated in the atmosphere above altitude 40 km, that is being contained in a column equivalent to not more than 100 m of air at sea-level, corresponds to a volume percentage of 10^{-3} to 10^{-4}, a value agreeing roughly with that calculated from Nernst's theorem for thermal equilibrium at 6000°. At concentrations of this order, the natural thermal decomposition of O_3 cannot be neglected as has been proposed, when explaining the decrease of O_3 towards the equator. It becomes also apparent in cyclonic, or anti-cyclonic, conditions, owing to the heat radiated to, or from, the troposphere. During the "ultra-violet outburst's" of the sun, as proposed for explaining auroras and magnetic storms, the ozone-building radiations could reach 6 times, the destructive radiations but 1.2 times their stationary values. The daily measurements recently made at Arosa, Marseille, Oxford, etc. do not exhibit an increase in O_3 for the few days preceding or following the strongest magnetic storms. (October 15, 1926, July 7/8, and October 18, 1928). If the outburst lasted only for one-half hour, the increase would have been smaller than the error of observation (0.01 cm); on the other hand, increases by 0.04 cm are observed in the absence of magnetic storms.

20. Electrodynamic damping in pulsating stars. ROSS GUNN, *Naval Research Laboratory, Washington, D. C.*—Small radial pulsations of stars are shown to be highly damped by electrodynamic forces when the star has a magnetic field. The author's theory of the permanent magnetic field of the sun indicates that the field is produced by regenerative means which is triggered off by a small initial field. The small initial field probably arises from the rotation of the star combined with a separation of charge, although it may conceivably arise in other ways. Thus rotating stars will have a magnetic field and cannot pulsate, and conversely stars which pulsate have no magnetic field and do not rotate. Cepheid variables are observed to pulsate and therefore have no magnetic field and do not rotate. This is in keeping with the idea that Cepheid variables, being youthful giants, are so large that they would be unstable under rotation. These considerations appear to remove the difficulties encountered by Eddington in his detailed theory of star pulsations.

21. The analysis of cosmic-ray observations. LE ROY D. WELD, *Coe College.*—Millikan and Cameron find evidence of several distinct absorption coefficients for the cosmic rays in deep lakes, suggesting a spectrum of definite wave-lengths. In this paper, a general method of least-square adjustment of non-linear observation equations is adapted to the analysis of the cosmic-ray absorption curve, in order to determine the most probable values of the two constants for each component of the radiation.

22. Mass-weight ratio of metals under strain. P. I. WOLD, *Union College.*—The late Dr. Charles F. Brush conducted work for years on the mass-weight ratio of metals. One of his methods of experimentation consisted in weighing certain alloys while they were subjected to very considerable pressure. He found losses in weight amounting to as much as one part in 40,000. Measurements have been carried on for the last two years on alloy specimens, which he had prepared, to see if independent observers could reproduce his results. On such specimens changes amounting to about one part in 150,000 were obtained. The curves of weight against pressure show the same characteristics as obtained by Dr. Brush. While the changes are small, they are substantially larger than can be ascribed to the errors of the balance or to temperature changes.

23. The surface tension of molten glass at temperatures near the melting point. W. B. PIETENPOL AND H. H. SCOTT, *University of Colorado.*—A new method has been devised by which the surface tensions of a number of glasses of different composition have been determined throughout a range of temperature of approximately 200°C. just above the softening points. The method is termed "The Bulb Method" and is similar to the soap bubble experiment in which the excess of pressure within the bubble can be balanced against a small head of liquid in a manometer. It was found that the weight of the glass bulb needed to be considered and a formula is developed giving the relation between surface tension and pressure in which the correction factor is introduced. Throughout the range to which the method is applicable, it is found that the surface tension of glass varies but slightly with temperature. The magnitude of the surface tension for different glasses is of the order of 250 to 350 dynes per cm.

24. Thermal expansion of lead. PETER HIDNERT AND W. T. SWEENEY, *Bureau of Standards.*—Data by Hidnert and Sweeney on the linear thermal expansion of one sample of cast lead and various lead-antimony alloys between 20 and 60°C were published in 1924 by Vinal, "Storage Batteries." Since then additional determinations were made on three samples of cast lead over various temperature ranges between 20 and 300°C. The following results were obtained:

		Average coefficients of linear expansion per Degree Centigrade				
Sample[1]	Lead content Percent	20 to 60°C. $\times 10^{-6}$	20 to 100°C. $\times 10^{-6}$	20 to 200°C. $\times 10^{-6}$	20 to 300°C. $\times 10^{-6}$	Difference in length before and after Expansion test Percent
1215[2]	99.8	29.0	28.9	29.7	30.9	−0.01
		——	28.8	29.4	31.0	.00
1144	99.9	28.3	28.6	29.5	31.2	.00
1001[3]	——	29.2	29.6	31.2	32.5	+ .02

[1] Samples 1215 and 1144 were cast in sand molds, and sample 1001 in a pre-heated steel mold.

[2] Values given on second horizontal line were obtained on a second test.

[3] Sample 1001 cast from same ingot as sample 1215.

The differences obtained in the coefficients of expansion are evidently due to variations in the methods of casting.

25. Two different types of association of alcohol molecules in the liquid state. G. W. STEWART. *University of Iowa.*—By x-ray diffraction studies of liquid alcohols, including twenty-one octyl alcohols, eleven primary n-alcohols, and nine additional isomers of primary normal alcohols, evidence is obtained of two types of association of molecules. When the OH group is attached to the terminal carbon atom or the one adjacent thereto, the molecules are associated primarily in pairs with the OH group adjoining and the median lines of two chains in the same line. At the same time there is a more or less orderly lateral arrangement of these pairs of OH groups. When the OH group is attached to any other carbon atom in the chain, then the double molecules disappear and the association is side by side. There is no exception to these conclusions in the liquids studied.

26. On the theory of the solar corona. E. O. HULBURT, *Naval Research Laboratory.*—The outer atmosphere of the sun is assumed to be composed mainly of charged particles, which are actuated by gravitation, radiation pressure and the magnetic field of the sun. By distillation along the lines of magnetic force the particles collect in the lower latitudes of the solar outer atmosphere and by their diamagnetism and drift currents reduce the magnetic field approximately to zero in this region, leaving a stray field at the poles. Thus the coronal streamers, prominent during sun-spot minima, are regarded as owing their form to the magnetic field of the sun. Whereas the wide-spreading structureless coronal luminosity expending out from the lower latitudes is due to an accumulation of ionization which reduces the magnetic field to a low value and permits the radiation to blow the particles out to great distances. During maximum solar activity there is sufficient ionization of the outer atmosphere to reduce the magnetic field to a low value even at the poles, and hence the outer atmospheric spray extends roughly equally in all directions, in accord with the appearance of the corona.

27. Resistance of an electrolytic conductor at various frequencies. D. E. RICHARDSON, *University of Chicago.* (*Introduced by J. Barton Hoag.*)—The resistance of a conductor, as defined by the ratio of electrical energy converted into heat and the square of the current, is a function of the frequency of the current because of the non-uniform current density throughout the cross-section of the conductor. Classical electrical theory offers an equation for this skin effect. This has been verified for metallic conductors for frequencies up to one megacycle. Using a calorimetric method, the equation is now verified in a particular case of electrolytic conduction (30% solution of H_2SO_4) for frequencies up to eight megacycles (37 m). It is concluded that the resistivity of this electrolytic conductor is independent of the frequency up to eight megacycles, since this assumption was made in the derivation of the equation. Measurements of the currents were made by comparing photometrically the intensities of two filaments, one carrying the high frequency currents, the other direct current.

28. Change of spacing of positive column striations with temperature. F. M. SPARKS AND CHAS. T. KNIPP, *University of Illinois.* Cassen (Phil. Mag. **268,** 948 (1926)) predicts that the separation of the striations in the positive column of a discharge tube should increase almost linearly with the absolute temperature. A discharge tube was heated in a liquid bath, the temperature range being from room temperature to 165°C. Hydrogen was used in the tube, but only the blue striations, due to impure hydrogen (Handbuch der Physik, vol. 14, p. 298) were obtained. To detect any temperature lag or any change in the characteristics of the gas the separations were noted with both increasing and decreasing temperature. The resulting curves showed no appreciable lag. Cassen's prediction is verified for the wide striations, at pressures around 1 mm Hg, but for the narrow striations, above 1.5 mm, the separation decreases with increasing temperature. However, the separation, in general, reaches a minimum value, and then begins to increase with increasing temperature. A series of temperature-separation curves were plotted for hydrogen at 2.5 mm, using three different values of current, after successive additions of impurity. The general shape of the curves remained the same, but were shifted to smaller values of separation, reaching a minimum, and then were shifted back to greater values.

29. A glass window mounting for withstanding pressures of 30,000 atmospheres. THOS. C. POULTER, *Iowa Wesleyan College.* The range in the field of optical study at high pressures has been extended from approximately 4,000 atmospheres to 30,000 atmospheres or even higher by the development of a window mounting that will withstand these higher pressures. This window mounting consists of a piece of glass 12 mm in diameter and 8 mm in thickness and having one of its flat surfaces placed over a 6 mm hole in a polished surface of hardened "high speed" steel disk. No gasket material is used between the steel and the glass. Since the flowing of the gasket material under pressure was the main source of unequal strains in the windows causing them to break, the piece of "high speed" steel is held in place by means of a large screw which in turn carries another window similarily mounted so as to catch flying materials in case the first window shatters.

30. Magnetostriction measurements us'ng a heterodyne beat method. A. B. BRYAN AND C. W. HEAPS, *The Rice Institute*. Two circuits oscillating with radio frequency produce a beat note which is itself made to beat slowly with a tuning fork. A photographic record of this slow beat is obtained on a moving photographic film. A parallel plate condenser in one of the oscillating circuits has its capacity changed by the magnetostriction of a nickel wire supporting one of the plates. From the photographic record the magnetostriction can be accurately determined. A search coil around the nickel wire picks up Barkhausen discontinuities which are then amplified and recorded on the film simultaneously with the magnetostriction effect and a time scale. Indications are that a Barkhausen discontinuity is accompanied by a sudden change in the length of the nickel wire. The apparatus detects a length change of about 10^{-7} cm in the length of the wire and can be used for a very rapid cycle of magnetization. Magnetostrictive hysteresis is to be investigated in different materials.

31. Diffraction of molecules. OTTO STERN, *Hamburg University*. (*Introduced by W. L. Severinghaus.*)

32. Deflection of hydrogen positive rays by calcite. A. J. DEMPSTER, *University of Chicago*. A series of photographs of the reflection patterns of hydrogen canal rays from a calcite crystal has been obtained with different angles of incidence showing a gradual alteration in the pattern with angle. Patterns have been obtained from three different calcite crystals. A charging up of the surface was observed in one case, as shown by the deflection of the negative ions in the canal ray beam. The amount of the deflection is of the order of magnitude required by the first of the Laue equations, $a(\alpha-\alpha_0)=\lambda$, if $\lambda=0.0017$A, as given by the de Broglie formula. The lines in the patterns in many cases form arcs of circles passing through the center. This suggests the reflection of the rays at the planes belonging to various zones as found with x-rays in Laue spot photographs. The angles at which reflection occurs when small are influenced very greatly by any surface energy or change of refractive index, even if very small. Radiation is excited in the calcite by the impact of the canal rays, which issues outside of a critical angle of approximately 0.01 radian with the surface. The refractive index deduced agrees with that of radiation of the wave-length of the Kα calcium line.

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